STUDY OF DEGRADABLE PLASTICS

EXECUTIVE SUMMARY

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A STUDY OF DEGRADABLE PLASTICS

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Report prepared by:
Ortech International

Report prepared for:
Waste Management Branch
Ontario Ministry of the Environment

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FORWARD

The recent introduction of degradable plastics into the marketplace has caused widespread controversy over the potential benefits and drawbacks of these products. Recognizing the need to put the matter into environmental and scientific perspective, EPIC (Environment and Plastic Institute of Canada) and the Ontario Ministry of the Environment agreed to jointly sponsor a third-party study to determine the effectiveness of degradable products. The study was to be based primarily on published, peer-reviewed, scientific literature. Opinion data was specifically to be excluded and media reports, of which there were many, were to be used as little as possible.

A number of universities and research organizations were invited to bid on the project. Of the bids received, ORTECH International was selected to do the study based on their well known expertise and credibility with industry and the Canadian public.

Coincident with the carrying out of the study, a multi-stakeholder Degradability Committee was formed within EPIC, consisting of plastics processors, raw material suppliers, and suppliers of degradable additives. One of the initial tasks of the Committee was to formulate a position statement (enclosed) to put into the best possible perspective the issues surrounding degradable plastics, and to better define their role in the management of plastic waste.

EXECUTIVE SUMMARY

Plastics have come under increasing attack by the public as a major contributor to litter and to solid waste disposal problems. Although plastic waste currently in North America comprises only about 7% of municipal solid wastes on a weight basis it is highly visible since it constitutes about 18% of the initial volume of municipal waste and may take many years to degrade when discarded as litter or to landfill sites.

As plastics have replaced other materials such as glass, metals and paper, the percentage of waste composed of plastics has nearly doubled in the years 1976 to 1984 from statistics published in the USA in 1988. This has lead to mounting concerns about plastics waste disposal. Options which could reduce litter and extend the life of existing solid waste disposal facilities such as separation and recycling of plastic wastes and the use of plastics which would degrade in the environment are now being considered.

The term "degradable" is generally used to identify a class of plastics which have been compounded or engineered to rapidly degrade in a relatively short period of time in the environment. These systems with claims for enhanced degradability presently fall into two groups "photodegradable" and "biodegradable". There is much debate as to the extent of degradation of biodegradable and photodegradable plastics under various environmental conditions.

As a result of these uncertainties on the performance of degradable plastics and their potential to alleviate the plastic waste and litter problems, the Environment and Plastics Institute of Canada and the Ontario Ministry of the Environment commissioned the present independent study to review the literature and obtain data from trade

journals and in particular, scientific data from peer-reviewed journals and the patent literature on commodity plastics which are claimed to photo or biodegrade.

The objective of the study was to determine if biodegradable plastic products and the residues of photodegradable plastics currently on the market are biodegradable with respect to time and process conditions in Ontario.

Literature Search

A computer assisted literature search of selected databases on the subjects of "biodegradability" and "photodegradability" of commodity plastics was carried out covering the period from the early 1970's to the present time (November 1989). The search uncovered many articles from trade journals, press releases and papers presented at conferences. These were useful in obtaining information on claims being made for the "degradable" plastic products by companies. Limited data, usually without experimental details, in the form of graphs and tables from in-house studies on product degradability were sometimes available from these sources along with proposed mechanisms for degradation.

Publications on "biodegradability" and "photodegradability" from refereed journals and from the patent literature were obtained and reviewed.

Definition of Degradable Plastics

The term "degradable plastics" implies that "normal" plastics are non-degradable which is not the case since all polymers will eventually

degrade in the environment although the process may take centuries to occur. However, because of their longevity, many would regard normal thermoplastic materials as "non-degradable" for all practical purposes. The term "degradable" is generally used to identify a class of plastics which have been compounded or engineered to rapidly degrade in a relatively short period of time in the environment. These enhanced degradable systems presently fall into two groups - "photodegradable" and "biodegradable".

There is a need for a definition of degradability if the performance of environmentally degradable plastics is to be assessed. In legal terms, degradability will require clear and unequivocal definition if misunderstanding of claims on "degradation" are to be avoided, but it is difficult to construct a practical chemical definition to meet this need. The concept of "degradable plastic" incorporates both chemical degradation of the polymer into shorter chains and the physical breakdown or deterioration of the plastic material into fragments. A recently proposed definition for degradable plastics by ASTM Subcommittee D20.96 on Environmentally Degradable Plastics incorporates both of these aspects and would apply to both biodegradable and photodegradable plastics *"Degradable Plastics: Plastic materials that undergo bond scission in the backbone of a polymer through chemical, biological and/or physical forces in the environment at a rate which is reasonably accelerated, as compared to a control, and which lead to fragmentation or disintegration of the plastics".*

In considering what constitutes satisfactory performance of a degradable plastic the terms of reference regarding product type and intended purpose or application, mode of disposal, expected environmental conditions and time frame should be specified if misinterpretation of claims for "degradability" are to be avoided. In addition there is a need to

define what are the intermediate products and end results of the degradation and deterioration processes when environmentally degradable plastics are discarded to the environment.

A common misconception in much of the earlier trade literature in the 1970's was that the entire degradable plastic material simply "disappeared". This reflected the belief that once decomposition of a disposable plastic had been initiated by the action of a photochemical, biological or chemical trigger, or combination of these, that the molecules split into smaller units which then became susceptible to normal processes of oxidation and decomposition by microorganisms and were completely converted to carbon dioxide and water. Later articles published in the mid to late 1980's generally present a more balanced viewpoint, reflecting the scientific evidence, that although products made of "degradable" plastics may lose their integrity and become less visible by breaking down into fragments or "plastic dust", assertions as to the ultimate fate of these plastic fragments are not now usually made.

The more recent patent filings and conference papers on both "biodegradable" and "photodegradable" plastic products also tend to focus more on claims and demonstrations of loss of strength, integrity and fragmentation of plastic compositions as the end-point after a period of exposure to environmental, or simulated environmental, conditions. The degradation products of these environmentally degradable polymers have not been characterized so that potential toxicity and environmental effects are largely unknown. While there is experimental evidence presented of degradation in terms of loss of strength, embrittlement and fragmentation of these formulations on exposure to environmental factors there is a need to define the rate at which this occurs and to quantify the end-points under specified test or environmental conditions in comparison to conventional plastic materials of the same type. For

example, statements that definitive and rapid disintegration times are not required for biodegradable garbage bags and shopping bags destined to end up in sanitary landfills presents a broad base for interpretation of environmental biodegradation claims for starch based plastics and leads to controversy.

In the case of photodegradable products the approaches taken by manufacturers to enhance the photodegradability of plastics all share the common objective of breaking long polymer chains down into shorter ones leading to embrittlement and subsequent break-up into small fragments by natural mechanical forces. Most bulk commodity plastics, in the absence of additives such as ultraviolet stabilizers and screening agents, are inherently photodegradable so that the difference between "non-photodegradable" and "photodegradable" plastics lies primarily in the length of exposure time to reach an embrittled state. The use of expressions such as "enhanced degradation", "accelerated decomposition", "are more easily or quickly degraded" in connection with photodegradable and/or biodegradable compositions are too vague and may lead to false expectations on the part of users particularly if legislation has been introduced mandating the use of "degradable" plastics for certain applications. In efforts to distinguish between "normal" and "enhanced photodegradable" products the concept of "controlled" lifetimes" or "programmed degradation" has been used in the patent literature to describe a product which remains essentially unchanged during its useful lifetime and then subsequently undergoes rapid degradation.

While this helps to distinguish between products with "normal" and "enhanced photodegradability" these claims also must be firmly linked to a large number of environmental factors such as humidity, temperature, UV wavelength (solar) and time of exposure if defined claims of controlled or enhanced photodegradability are to be developed.

Biodegradation of Degradable Plastics

High molecular weight synthetic polymers containing a largely C-C backbone as a class are generally resistant to biodegradation. Exceptions are polymers with aliphatic esters in the main chain such as ε-caprolactone and polyurethanes based on polyester diols. Lower molecular weight hydrocarbons are more susceptible to attack by microorganisms.

Evidence published to date only indicates that under certain conditions polymer compositions with photodegradable and/or biodegradable claims will lose their integrity and fragment. Most of the recent commercial research and development appears to have been directed towards development of systems with a built-in package of pro-oxidant(s) and oxidizable and/or biodegradable components which can more predictably result in deterioration and fragmentation of the plastic product at the end of its useful life when buried in soil or discarded to landfill or composting operations.

The biodegradability of a number of commercial plastics used for packaging based on polyethylene, polystyrene and polyvinyl chloride was investigated in the 1970's. Using fungal growth tests and soil burial tests it was shown that the polymer itself is not attacked. An investigation of the effect of polymer molecular weight and branching indicated that for linear hydrocarbon samples only those samples with molecular weights up to about 450 (C_{32}) were susceptible to microbial attack. Above that no microbial growth was observed. Branched hydrocarbons with molecular weights less than 450 were not attacked.

More recent work carried out in 1988 with oligomers of polyethylene ($C_{28}H_{58}$, $C_{32}H_{60}$ and $C_{30}H_{74}$) also found biodegradation to be

dependent on molecular weight. Test methods using bacteria rather than fungi also indicate that the upper limit for growth on ethylene oligomers is about 600-800 and on styrene 200-300; butadiene 500 and isoprene 400-1000.

The photoxidation of polyolefins has been shown to result in chain shortening and altered surface morphologies containing ketone groups. The biodegradability of ketones of increasing molecular weight has therefore, been investigated and reported in the literature. Again it was found that the growth rate decreased with increasing molecular weight although middle ketones up to C_{35} (MW>500) were still attacked.

The common commodity polyolefins contain small amounts of oligomer, the amounts depending on manufacturing and processing conditions, which give evidence of a minimal amount of microbial growth when the intact polymer is challenged. If the oligomer is separated and challenged as a separate fraction it supports microbial growth and the high polymer from which the oligomers have been extracted does not support growth. UV irradiation of polymers will increase the amount of oligomer but probably not in excess of a limiting value determined by kinetic factors involved in oligomer formation and degradation. Evidence is that it is the oligomer fraction of photolyzed olefins that is susceptible to attack by microorganisms. The chemical catalytic oxidation or photoxidation of plastics leading to embrittlement and, through the action of mechanical forces, the production of a fine plastic powder or plastic "dust" results in the polymer having a greatly increased surface area.
It has been claimed by some authors that these finely divided polymers undergo enhanced and progressive attack by microorganisms and their extra-cellular enzymes. There is however, no evidence that the high polymer itself will undergo progressive attack as the result of any

mechanical dispersion at the supramolecular level. The appearance of enhanced microbial growth on finely divided polymers is due to more rapid diffusion of the oligomer to particle surfaces.
There is therefore agreement in the literature that unless polymers are degraded to low molecular weight fractions (MW<1000 average) little or no biodegradation can take place as evidenced by plate growth tests or soil burial.

Products of Breakdown of Plastics with Enhanced Degradability

Concern has been expressed that the degradation or partial degradation products of degradable plastics may constitute a pollution problem. The literature search did not reveal any studies which had been specifically designed to look at this problem. This is not surprising since the problem is a complex one. The first difficulty lies in characterizing the starting material as most polymers exist as statistical mixtures of chains of varying lengths. Depending on the method of synthesis these chains may, in addition, have varying numbers of smaller side chains branching out from them. The composition of the polymer chains may also vary considerably. Gross chemical analysis of unfractionated products will, under these circumstances, yield only averaged compositional data. Commodity plastics such as the polyolefins are also often characterized by highly crystalline regions where the polymer chains exist in close packed arrangements surrounded by more highly amorphous regions with the chains in a greater state of randomness with respect to their mutual orientation.

Chemical reactions, such as photochemical reactions, which are dependent upon various types of molecular motion will generally take place more readily in the amorphous regions.

The second major difficulty lies in the many damaging factors responsible for the environmental degradation of polymers. These may

be classified as mainly thermo, thermo-oxidative, photo, photo-oxidative, chemical, hydrolytic and biological degradation.
Depending on the environment one or more of these factors may predominate. For example, plastic litter is likely to be subject to photo, photo-oxidative and thermal effects while plastic bags in compost piles would be subject to mainly thermal and thermo-oxidative effects initially. These factors are likely to lead to the following degradation processes: random chain scission, depolymerization, cross-linking, side group elimination or substitution and reactions of side groups among themselves. These basic types of degradation processes seldom take place separately and the simultaneous application of many damaging factors in the environment makes evaluation of the degradation process very difficult.

In the case of the photodegradation of plastics a great deal is understood about the general mechanisms of polymer photodegradation and photo-oxidation, but what is lacking is knowledge of the chemical species formed and at what rate these are produced. In the case of normal polyethylene subjected to UV in the presence of oxygen, ketones, aldehydes, carboxylic acids, esters, peroxide compounds, ethers, alcohols and low molecular weight alkanes have been listed as by-products. Additional by-product complexities resulting from simultaneous application of damaging factors in the environment and from the action of photosensitizers in photodegradable plastics are likely.

Other products which might be leached or released on degradation in the environment are metals such as nickel, cobalt, copper and iron, anti-oxidants, pro-oxidant or activator residues, UV stabilizers and heat stabilizers. There is also production and loss of volatiles during

photodegradation and some of these may be branched short chain hydrocarbons which would be resistant to biological attack.

While that portion of the polymer which has been degraded to a linear polymer of molecular weight less than 1,000 may be subjected to attack by microorganisms there is no information on the intermediate or end metabolites resulting from this or on the effects of the accumulation of quantities of plastic "dust" or fragmented residues resulting from plastics degradation in the environment.

The latter, consisting of tiny fragments of the original polymer plus partially degraded or even cross-linked polymer may merely act as a soil amender or conditioner and behave in a similar fashion to humic materials in soil. If however, the material contains reactive end groupings such as carboxylic acid, ketone or alcohol grouping the material may be leached through the soil as say the metal salt of a long chain carboxylic acid and become a ground water pollutant. No information on the characterization and fate of any of these partially degraded polymeric materials appears to have been published in refereed journals. Nor were references found which claim that by-products are definitely toxic or harmful.

The rate of degradation of the various photodegradable plastics currently available are dependent upon the amounts of sensitizing agents incorporated as well as exposure levels to UV light of 330 nm wavelength or less. In a laboratory setting with controlled conditions using appropriate lamps and filters the time required to achieve a given degree of polymer degradation can be reasonably predicted. In an outdoor environment there are a large number of factors which can affect the amount of light absorbed per unit time and hence the lifetimes. Such factors include average temperatures, rainfall and humidity, wavelength, distribution of the solar radiation at the particular location as well as its angle of incidence. Effects of shading by leaves from growing crops for

example on degradable mulching film or on degradable plastic litter located partially in shade and the effects of dirt, colouring pigments etc. may all delay photodegradation.

The failure of photodegradable agricultural mulch film to penetrate the British market has been ascribed to the va iable and low intensity of the ultraviolet light. The greater predictability to UV exposure could also account for the relative success of photodegradable agricultural mulch film in Israel and in the state of Florida. "Controlled" lifetime for degradable plastics outdoors in certain geographic locations for applications such as mulch films is therefore uncertain.

In the case of "biodegradable" plastics the environmental variables affecting degradation and product performance are also difficult to predict. In landfill operations some thirty environmental variables affecting sanitary landfill degradation of municipal waste have been identified. Factors such as moisture, temperature, numbers, types and physiological state of organisms present in the vicinity of the particle, degree of anaerobiosis, micro-nutrients and soluble metals are likely important factors.

Moisture is usually the chief limiting factor for biodegradation of materials. Most landfills are designed to minimize water infiltration unless leachate control and recycle are practiced. Landfills, as presently operated, in general act more as burial tombs than as bioreactors. Biodegradation of putrescible materials does take place to some extent as evidenced by methane production. This is far from optimal in most circumstances and continues at a slow and sometimes unpredictable rate for many years.

A fair description of what happens in sanitary landfills as presently operated is summarized in a recent statement that "biodegradation (of plastics) may have only marginal benefit since it (landfill) does not

remove all materials or even biodegradable materials in a reasonable time".

Indication of slow degradation of plastics has, however, been obtained in recent studies from 17 to 20 year old municipal landfill sites. Using bomb calorimetry to determine the BTU value of recovered polyethylene samples and comparing the values with virgin polyethylene to determine the degree of degradation it was found that 93% of samples showed degradation, with 30% of the samples degraded 10% or more.

Recent work at the University of Missouri in a six month study of polyethylene film, with and without 6 percent starch indicated that starch was largely removed from the polyethylene when exposed to conditions simulating landfill, compost heap and anaerobic waste sludge digester and surface litter environments. Most rapid removal was under anaerobic waste treatment conditions and slowest in air.

It was also reported that "the polyethylene degraded to smaller molecules" particularly under anaerobic conditions where decomposition was greatest and that up to 15% of the 1200 carbon-long molecules gradually decayed into 25-carbon waxes.

If these observations under anaerobic digester conditions are confirmed a much more rapid decomposition of plastics might be obtained in landfills if sufficient amounts of water are permitted in a sanitary landfill operation to maximize decomposition under anaerobic conditions.

Studies in Sweden of normal and photodegradable ^{14}C labeled plastics which had been exposed to UV radiation and placed in soil disclosed relatively low rates of biodegradation. Less than 10% biodegradation of UV exposed/UV sensitized polyethylene in 10 years in soil was noted even though the final level of degradation appeared to be close to a decomposed structure. Other studies using ^{14}C labeled polyethylene in

soil with higher moisture content indicated a somewhat higher rate of about 2% per year. This latter figure would correspond to the highest levels of degradation (approximately 50% in 20 years) noted in some polyethylene samples recovered in the landfill site studies.

In the case of composting operations there is a greater attempt to control the environment for biological decomposition under aerobic conditions. Initial moisture contents of 50-60% and operating temperatures of 55-60°C at oxygen concentrations of 5 to 15% and a pH of 6 to 8 are considered optimal.

Several studies have been undertaken recently on the use of biodegradable polyethylene bags for the collection of yard wastes for composting. One trial underway in Nebraska is using bags which contain 6% cornstarch, a photodegradable chemical and a pro-oxidant which are said to make the bag more susceptible to oxidation and heat decomposition.

Preliminary results after five weeks of windrow composting at 60°C indicated that the bag material appeared to have lost strength and it was estimated that the bags will degrade in 18 months. Normally the time required for the active stage of composting of municipal waste by the windrow method is 2 to 6 months. A period of 18 months for bags to "degrade" would therefore require a considerable post-composting curing period to allow this to occur.

Testing of Degradable Plastics

In addition to the need for agreement on definitions of "photodegradable" and "biodegradable" plastics the literature search revealed that there is a need for standardization of test environments and test methods if the performance of degradable plastics is to be assessed more fully. At the present time ASTM Subcommittee D20-96 on Environmentally Degradable Plastics is reviewing these needs and has started to address the standardization issues.

Test environments need to be characterized, be reproducible and relate to the intended purpose and fate of the degradable plastic material. Accelerated laboratory tests which show correlation to field environmental conditions would be preferable. Comparison with the behaviour of a well characterized "normal" plastic and with known biodegradable polymers such as polycaprolactone or cellulose under the conditions of the test environment may be one method of achieving this for evaluation of biodegradable plastics. The starting test materials also need to be well characterized before testing. Similar requirements would apply to plastics with photodegradable claims.

Standardization of test methods for measuring changes in physical and chemical properties during exposure and the rate at which these occur in the test environments are also required. These may range from simple measurement of weight loss as a measure of volatilization to on-line measurement of carbon dioxide and methane production using a biometer to measure rates of true biodegradation. There is also a need to quantify the end-point or end points of degradation if "degraded" is to be defined for photodegradable, biodegradable and photo-biodegradable plastics.

Further research to characterize the intermediate products and end products of plastics with enhanced degradation claims is required.

Possible toxic or adverse environmental effects of these degradation or partial degradation products also requires investigation.

Key Findings from the Literature

1) There are no universally accepted definitions of biodegradable or photodegradable plastics. The American Society for Testing Materials (ASTM) and the Canadian Standards Association (CSA) are addressing this issue.

2) There are currently no universally accepted standards or test methods for evaluating the performance of degradable plastics. ASTM and CSA are addressing these issues.

3) It is recognized that an accelerated loss of physical properties of plastics can be induced through the addition of certain additives. Conventional plastics also degrade although the time required is substantially longer. Consequently any reference to controlled lifetimes of degradable plastics is a relative rather than an absolute term.

4) There is agreement in the literature that unless polymers such as polyethylene are degraded to low molecular weight straight chain alkane fractions (molecular weight less than 1,000 average) little or no biodegradation can take place as evidenced by microbial plate growth tests or soil burial tests. Branching of the alkane chains appears to prevent biodegradation regardless of molecular weight. Most studies on biodegradability have been carried out on polyethylene and little data are available on other commodity plastics such as polystyrene.

5) There is very little information on the by-products or end-products resulting from degradation of either conventional plastics or plastics with enhanced degradation. The fate of these

degradation products is largely unknown. In addition, little is known about the potential effects of release of plastics additives, for example, organometallic antioxidants, on degradation of the packaging. As a result the environmental impact cannot be assessed at this time.

6) The effects of degradable plastics on the recyclability of plastics is unknown. Further study and research is required in this area.

PLASTICS DEGRADABILITY

WHY DEGRADABILITY

The growing world wide concern over solid waste has caused a great deal of attention to be focussed on plastics, which are perceived to be non "degradable". Products are now being marketed which claim to address this perceived deficiency in plastics, and while these products will find some applications, they are by no means a universal solution to the plastics waste problem. A lack of understanding of the waste and litter problem has created a great deal of confusion in the minds of the general public. The roles that "degradable plastics" can and cannot play are discussed below.

WHAT IS DEGRADABILITY

All plastics deteriorate and break down over time. Scientists have expended a great deal of effort, over the years, to improve the durability of plastics and extend the useful life of plastic products. Much of the durability improvement is achieved with the use of additives.

The new products offered as degradable are in fact designed to do the very opposite i.e. speed up the degradation or breakdown of the product.

Two general types of degradable products are being offered. Photodegradable products exhibit accelerated degradation when exposed to sunlight. Products which are commonly called biodegradable contain cornstarch which depends on the action of micro organisms, and other chemicals, which promote breakdown of the plastic. In both cases, under the correct conditions, it results in the breakdown of the plastic article into ever smaller pieces.

EFFECT ON LITTER

Litter is the result of irresponsible or accidental disposal of products. The ideal way to eliminate litter is to eliminate the littering behaviour through education and deterents such as fines, and to identify and correct the causes of accidental littering.

Given that litter does occur, it contributes to visual pollution and poses a potential threat to wildlife. In addition to education to change behaviour, there is a need to either collect the litter or to reduce the longevity of littered items.

While there is currently no legislation in Canada, in many foreign jurisdictions (i.e. Italy, Florida), certain plastic packaging materials are being mandated to lose properties (degrade) within specified time frames (within120 days for polyethylene, within one year for polystyrene, etc.)

Photodegradable products can have a positive impact on plastics litter in both land and marine situations. The breakdown of plastics is triggered by ultra violet radiation from the sun. The effectiveness is dependent on exposure intensity and will vary with factors such as the season, geography, dirt or water cover, shading, etc. The question of whether making plastics degradable will encourage littering has frequently been asked but remains unanswered.

Available commercial biodegradable products are not being promoted for litter management due to the significant difficulties in consistently achieving the needed conditions for biological activity.

EFFECT ON LANDFILL

Degradation is generally a complex and slow process. For a material to biodegrade, it must be exposed to the correct combination of acidity, temperature, nutrients, particle size, moisture, air and bacteria. Under modern landfill conditions, many materials generally regarded as degradable (i.e. food, yard waste, paper, etc.) deteriorate either slowly or not at all. Coatings or heavy printing further slow down the degradation rate.

Photodegradable plastic systems are not being promoted as a means to reduce landfill because the ultra violet light needed to cause degradation is not present.

Under the correct conditions, the physical properties of plastics containing biodegradable additives can be reduced. However, sanitary landfills are typically run in a "dry" mode (i.e. clay cap, removal of leachate). This results in insufficient moisture for large scale degradation to occur.

In view of these conditions, the addition of biodegradable materials of any type will not extend the useful life of landfill sites.

PRODUCTS OF DEGRADATION

There have been questions raised about the environmental impact of the products of degradation and the increased rate at which additives such as pigments are released. These issues are being addressed through both supplier and industry-backed studies.

COMPATABILITY WITH RECYCLING

Questions have been raised about the compatability of degradable systems with recycling. The questions relate to the processability of the recycled plastics as well as possible reduced life of products made from recycled plastics. The effects depend on which degradable system is used, the type of recycling process, as well as the end product. These concerns are being addressed through further research.

ECONOMIC IMPACT

The use of degradable systems adds cost. The actual cost increase depends on the application and system chosen. The major cost increase components are in the cost of the additive system and, in the case of the biodegradable product, there may be additional plastic resin required.

QUALITY

The industry is concerned about the lack of recognized performance standards governing the use of degradable plastics. The Society of the Plastics Industry is working with organizations such as the Canadian Standards Association to address this need.

SUMMARY

Degradable plastics offer benefits in selected applications. Photodegradability may be useful in products with high litter potential. Biodegradable products may be beneficial in products which are not going to be recycled and which will be disposed of under conditions conducive to biodegradation. Research is continuing to determine the environmental acceptability of the products of degradation, and the impact on recycling and people's tendency to litter. It is important to recognize that degradability is only one component of responsible solid waste and litter management.

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A Study of Degradable Plastics

A Report to:

Environment and Plastics Institute of Canada
and the Ministry of the Environment, Ontario

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EXECUTIVE SUMMARY

Plastics have come under increasing attack by the public as a major contributor to litter and to solid waste disposal problems. Although plastic waste currently in North America comprises only about 7% of municipal solid wastes on a weight basis it is highly visible since it constitutes about 18% of the initial volume of municipal waste and may take many years to degrade when discarded as litter or to landfill sites.

As plastics have replaced other materials such as glass, metals and paper, the percentage of waste composed of plastics has nearly doubled in the years 1976 to 1984 from statistics published in the USA in 1988. This has lead to mounting concerns about plastics waste disposal. Options which could reduce litter and extend the life of existing solid waste disposal facilities such as separation and recycling of plastic wastes and the use of plastics which would degrade in the environment are now being considered.

The term "degradable" is generally used to identify a class of plastics which have been compounded or engineered to rapidly degrade in a relatively short period of time in the environment. These systems with claims for enhanced degradability presently fall into two groups "photodegradable" and "biodegradable". There is much debate as to the extent of degradation of biodegradable and photodegradable plastics under various environmental conditions.

As a result of these uncertainties on the performance of degradable plastics and their potential to alleviate the plastic waste and litter problems, the Environment and Plastics Institute of Canada and the Ontario Ministry of the Environment commissioned the present independent study to review the literature and obtain data from trade

journals and in particular, scientific data from peer-reviewed journals and the patent literature on commodity plastics which are claimed to photo or biodegrade.

The objective of the study was to determine if biodegradable plastic products and the residues of photodegradable plastics currently on the market are biodegradable with respect to time and process conditions in Ontario.

Literature Search

A computer assisted literature search of selected databases on the subjects of "biodegradability" and "photodegradability" of commodity plastics was carried out covering the period from the early 1970's to the present time (November 1989). The search uncovered many articles from trade journals, press releases and papers presented at conferences. These were useful in obtaining information on claims being made for the "degradable" plastic products by companies. Limited data, usually without experimental details, in the form of graphs and tables from in-house studies on product degradability were sometimes available from these sources along with proposed mechanisms for degradation.

Publications on "biodegradability" and "photodegradability" from refereed journals and from the patent literature were obtained and reviewed.

Definition of Degradable Plastics

The term "degradable plastics" implies that "normal" plastics are non-degradable which is not the case since all polymers will eventually

degrade in the environment although the process may take centuries to occur. However, because of their longevity, many would regard normal thermoplastic materials as "non-degradable" for all practical purposes. The term "degradable" is generally used to identify a class of plastics which have been compounded or engineered to rapidly degrade in a relatively short period of time in the environment. These enhanced degradable systems presently fall into two groups - "photodegradable" and "biodegradable".

There is a need for a definition of degradability if the performance of environmentally degradable plastics is to be assessed. In legal terms, degradability will require clear and unequivocal definition if misunderstanding of claims on "degradation" are to be avoided, but it is difficult to construct a practical chemical definition to meet this need. The concept of "degradable plastic" incorporates both chemical degradation of the polymer into shorter chains and the physical breakdown or deterioration of the plastic material into fragments. A recently proposed definition for degradable plastics by ASTM Subcommittee D20.96 on Environmentally Degradable Plastics incorporates both of these aspects and would apply to both biodegradable and photodegradable plastics *"Degradable Plastics: Plastic materials that undergo bond scission in the backbone of a polymer through chemical, biological and/or physical forces in the environment at a rate which is reasonably accelerated, as compared to a control, and which lead to fragmentation or disintegration of the plastics"*.

In considering what constitutes satisfactory performance of a degradable plastic the terms of reference regarding product type and intended purpose or application, mode of disposal, expected environmental conditions and time frame should be specified if misinterpretation of claims for "degradability" are to be avoided. In addition there is a need to

define what are the intermediate products and end results of the degradation and deterioration processes when environmentally degradable plastics are discarded to the environment.

A common misconception in much of the earlier trade literature in the 1970's was that the entire degradable plastic material simply "disappeared". This reflected the belief that once decomposition of a disposable plastic had been initiated by the action of a photochemical, biological or chemical trigger, or combination of these, that the molecules split into smaller units which then became susceptible to normal processes of oxidation and decomposition by microorganisms and were completely converted to carbon dioxide and water. Later articles published in the mid to late 1980's generally present a more balanced viewpoint, reflecting the scientific evidence, that although products made of "degradable" plastics may lose their integrity and become less visible by breaking down into fragments or "plastic dust", assertions as to the ultimate fate of these plastic fragments are not now usually made.

The more recent patent filings and conference papers on both "biodegradable" and "photodegradable" plastic products also tend to focus more on claims and demonstrations of loss of strength, integrity and fragmentation of plastic compositions as the end-point after a period of exposure to environmental, or simulated environmental, conditions. The degradation products of these environmentally degradable polymers have not been characterized so that potential toxicity and environmental effects are largely unknown. While there is experimental evidence presented of degradation in terms of loss of strength, embrittlement and fragmentation of these formulations on exposure to environmental factors there is a need to define the rate at which this occurs and to quantify the end-points under specified test or environmental conditions in comparison to conventional plastic materials of the same type. For

example, statements that definitive and rapid disintegration times are not required for biodegradable garbage bags and shopping bags destined to end up in sanitary landfills presents a broad base for interpretation of environmental biodegradation claims for starch based plastics and leads to controversy.

In the case of photodegradable products the approaches taken by manufacturers to enhance the photodegradability of plastics all share the common objective of breaking long polymer chains down into shorter ones leading to embrittlement and subsequent break-up into small fragments by natural mechanical forces. Most bulk commodity plastics, in the absence of additives such as ultraviolet stabilizers and screening agents, are inherently photodegradable so that the difference between "non-photodegradable" and "photodegradable" plastics lies primarily in the length of exposure time to reach an embrittled state. The use of expressions such as "enhanced degradation", "accelerated decomposition", "are more easily or quickly degraded" in connection with photodegradable and/or biodegradable compositions are too vague and may lead to false expectations on the part of users particularly if legislation has been introduced mandating the use of "degradable" plastics for certain applications. In efforts to distinguish between "normal" and "enhanced photodegradable" products the concept of "controlled" lifetimes" or "programmed degradation" has been used in the patent literature to describe a product which remains essentially unchanged during its useful lifetime and then subsequently undergoes rapid degradation.

While this helps to distinguish between products with "normal" and "enhanced photodegradability" these claims also must be firmly linked to a large number of environmental factors such as humidity, temperature, UV wavelength (solar) and time of exposure if defined claims of controlled or enhanced photodegradability are to be developed.

Biodegradation of Degradable Plastics

High molecular weight synthetic polymers containing a largely C-C backbone as a class are generally resistant to biodegradation. Exceptions are polymers with aliphatic esters in the main chain such as ε-caprolactone and polyurethanes based on polyester diols. Lower molecular weight hydrocarbons are more susceptible to attack by microorganisms.

Evidence published to date only indicates that under certain conditions polymer compositions with photodegradable and/or biodegradable claims will lose their integrity and fragment. Most of the recent commercial research and development appears to have been directed towards development of systems with a built-in package of pro-oxidant(s) and oxidizable and/or biodegradable components which can more predictably result in deterioration and fragmentation of the plastic product at the end of its useful life when buried in soil or discarded to landfill or composting operations.

The biodegradability of a number of commercial plastics used for packaging based on polyethylene, polystyrene and polyvinyl chloride was investigated in the 1970's. Using fungal growth tests and soil burial tests it was shown that the polymer itself is not attacked. An investigation of the effect of polymer molecular weight and branching indicated that for linear hydrocarbon samples only those samples with molecular weights up to about 450 (C_{32}) were susceptible to microbial attack. Above that no microbial growth was observed. Branched hydrocarbons with molecular weights less than 450 were not attacked.

More recent work carried out in 1988 with oligomers of polyethylene ($C_{28}H_{58}$, $C_{32}H_{60}$ and $C_{30}H_{74}$) also found biodegradation to be

dependent on molecular weight. Test methods using bacteria rather than fungi also indicate that the upper limit for growth on ethylene oligomers is about 600-800 and on styrene 200-300; butadiene 500 and isoprene 400-1000.

The photoxidation of polyolefins has been shown to result in chain shortening and altered surface morphologies containing ketone groups. The biodegradability of ketones of increasing molecular weight has therefore, been investigated and reported in the literature. Again it was found that the growth rate decreased with increasing molecular weight although middle ketones up to C_{35} (MW>500) were still attacked.

The common commodity polyolefins contain small amounts of oligomer, the amounts depending on manufacturing and processing conditions, which give evidence of a minimal amount of microbial growth when the intact polymer is challenged. If the oligomer is separated and challenged as a separate fraction it supports microbial growth and the high polymer from which the oligomers have been extracted does not support growth. UV irradiation of polymers will increase the amount of oligomer but probably not in excess of a limiting value determined by kinetic factors involved in oligomer formation and degradation. Evidence is that it is the oligomer fraction of photolyzed olefins that is susceptible to attack by microorganisms. The chemical catalytic oxidation or photoxidation of plastics leading to embrittlement and, through the action of mechanical forces, the production of a fine plastic powder or plastic "dust" results in the polymer having a greatly increased surface area.
It has been claimed by some authors that these finely divided polymers undergo enhanced and progressive attack by microorganisms and their extra-cellular enzymes. There is however, no evidence that the high polymer itself will undergo progressive attack as the result of any

mechanical dispersion at the supramolecular level. The appearance of enhanced microbial growth on finely divided polymers is due to more rapid diffusion of the oligomer to particle surfaces.
There is therefore agreement in the literature that unless polymers are degraded to low molecular weight fractions (MW<1000 average) little or no biodegradation can take place as evidenced by plate growth tests or soil burial.

Products of Breakdown of Plastics with Enhanced Degradability

Concern has been expressed that the degradation or partial degradation products of degradable plastics may constitute a pollution problem. The literature search did not reveal any studies which had been specifically designed to look at this problem. This is not surprising since the problem is a complex one. The first difficulty lies in characterizing the starting material as most polymers exist as statistical mixtures of chains of varying lengths. Depending on the method of synthesis these chains may, in addition, have varying numbers of smaller side chains branching out from them. The composition of the polymer chains may also vary considerably. Gross chemical analysis of unfractionated products will, under these circumstances, yield only averaged compositional data. Commodity plastics such as the polyolefins are also often characterized by highly crystalline regions where the polymer chains exist in close packed arrangements surrounded by more highly amorphous regions with the chains in a greater state of randomness with respect to their mutual orientation.

Chemical reactions, such as photochemical reactions, which are dependent upon various types of molecular motion will generally take place more readily in the amorphous regions.

The second major difficulty lies in the many damaging factors responsible for the environmental degradation of polymers. These may

be classified as mainly thermo, thermo-oxidative, photo, photo-oxidative, chemical, hydrolytic and biological degradation.
Depending on the environment one or more of these factors may predominate. For example, plastic litter is likely to be subject to photo, photo-oxidative and thermal effects while plastic bags in compost piles would be subject to mainly thermal and thermo-oxidative effects initially. These factors are likely to lead to the following degradation processes: random chain scission, depolymerization, cross-linking, side group elimination or substitution and reactions of side groups among themselves. These basic types of degradation processes seldom take place separately and the simultaneous application of many damaging factors in the environment makes evaluation of the degradation process very difficult.

In the case of the photodegradation of plastics a great deal is understood about the general mechanisms of polymer photodegradation and photo-oxidation, but what is lacking is knowledge of the chemical species formed and at what rate these are produced. In the case of normal polyethylene subjected to UV in the presence of oxygen, ketones, aldehydes, carboxylic acids, esters, peroxide compounds, ethers, alcohols and low molecular weight alkanes have been listed as by-products. Additional by-product complexities resulting from simultaneous application of damaging factors in the environment and from the action of photosensitizers in photodegradable plastics are likely.

Other products which might be leached or released on degradation in the environment are metals such as nickel, cobalt, copper and iron, anti-oxidants, pro-oxidant or activator residues, UV stabilizers and heat stabilizers. There is also production and loss of volatiles during

photodegradation and some of these may be branched short chain hydrocarbons which would be resistant to biological attack.

While that portion of the polymer which has been degraded to a linear polymer of molecular weight less than 1,000 may be subjected to attack by microorganisms there is no information on the intermediate or end metabolites resulting from this or on the effects of the accumulation of quantities of plastic "dust" or fragmented residues resulting from plastics degradation in the environment.

The latter, consisting of tiny fragments of the original polymer plus partially degraded or even cross-linked polymer may merely act as a soil amender or conditioner and behave in a similar fashion to humic materials in soil. If however, the material contains reactive end groupings such as carboxylic acid, ketone or alcohol grouping the material may be leached through the soil as say the metal salt of a long chain carboxylic acid and become a ground water pollutant. No information on the characterization and fate of any of these partially degraded polymeric materials appears to have been published in refereed journals. Nor were references found which claim that by-products are definitely toxic or harmful.

The rate of degradation of the various photodegradable plastics currently available are dependent upon the amounts of sensitizing agents incorporated as well as exposure levels to UV light of 330 nm wavelength or less. In a laboratory setting with controlled conditions using appropriate lamps and filters the time required to achieve a given degree of polymer degradation can be reasonably predicted. In an outdoor environment there are a large number of factors which can affect the amount of light absorbed per unit time and hence the lifetimes. Such factors include average temperatures, rainfall and humidity, wavelength, distribution of the solar radiation at the particular location as well as its angle of incidence. Effects of shading by leaves from growing crops for

example on degradable mulching film or on degradable plastic litter located partially in shade and the effects of dirt, colouring pigments etc. may all delay photodegradation.

The failure of photodegradable agricultural mulch film to penetrate the British market has been ascribed to the variable and low intensity of the ultraviolet light. The greater predictability to UV exposure could also account for the relative success of photodegradable agricultural mulch film in Israel and in the state of Florida. "Controlled" lifetime for degradable plastics outdoors in certain geographic locations for applications such as mulch films is therefore uncertain.

In the case of "biodegradable" plastics the environmental variables affecting degradation and product performance are also difficult to predict. In landfill operations some thirty environmental variables affecting sanitary landfill degradation of municipal waste have been identified. Factors such as moisture, temperature, numbers, types and physiological state of organisms present in the vicinity of the particle, degree of anaerobiosis, micro-nutrients and soluble metals are likely important factors.

Moisture is usually the chief limiting factor for biodegradation of materials. Most landfills are designed to minimize water infiltration unless leachate control and recycle are practiced. Landfills, as presently operated, in general act more as burial tombs than as bioreactors. Biodegradation of putrescible materials does take place to some extent as evidenced by methane production. This is far from optimal in most circumstances and continues at a slow and sometimes unpredictable rate for many years.

A fair description of what happens in sanitary landfills as presently operated is summarized in a recent statement that "biodegradation (of plastics) may have only marginal benefit since it (landfill) does not

remove all materials or even biodegradable materials in a reasonable time".

Indication of slow degradation of plastics has, however, been obtained in recent studies from 17 to 20 year old municipal landfill sites. Using bomb calorimetry to determine the BTU value of recovered polyethylene samples and comparing the values with virgin polyethylene to determine the degree of degradation it was found that 93% of samples showed degradation, with 30% of the samples degraded 10% or more.

Recent work at the University of Missouri in a six month study of polyethylene film, with and without 6 percent starch indicated that starch was largely removed from the polyethylene when exposed to conditions simulating landfill, compost heap and anaerobic waste sludge digester and surface litter environments. Most rapid removal was under anaerobic waste treatment conditions and slowest in air.

It was also reported that "the polyethylene degraded to smaller molecules" particularly under anaerobic conditions where decomposition was greatest and that up to 15% of the 1200 carbon-long molecules gradually decayed into 25-carbon waxes.

If these observations under anaerobic digester conditions are confirmed a much more rapid decomposition of plastics might be obtained in landfills if sufficient amounts of water are permitted in a sanitary landfill operation to maximize decomposition under anaerobic conditions.

Studies in Sweden of normal and photodegradable ^{14}C labeled plastics which had been exposed to UV radiation and placed in soil disclosed relatively low rates of biodegradation. Less than 10% biodegradation of UV exposed/UV sensitized polyethylene in 10 years in soil was noted even though the final level of degradation appeared to be close to a decomposed structure. Other studies using ^{14}C labeled polyethylene in

soil with higher moisture content indicated a somewhat higher rate of about 2% per year. This latter figure would correspond to the highest levels of degradation (approximately 50% in 20 years) noted in some polyethylene samples recovered in the landfill site studies.

In the case of composting operations there is a greater attempt to control the environment for biological decomposition under aerobic conditions. Initial moisture contents of 50-60% and operating temperatures of 55-60°C at oxygen concentrations of 5 to 15% and a pH of 6 to 8 are considered optimal.

Several studies have been undertaken recently on the use of biodegradable polyethylene bags for the collection of yard wastes for composting. One trial underway in Nebraska is using bags which contain 6% cornstarch, a photodegradable chemical and a pro-oxidant which are said to make the bag more susceptible to oxidation and heat decomposition.

Preliminary results after five weeks of windrow composting at 60°C indicated that the bag material appeared to have lost strength and it was estimated that the bags will degrade in 18 months. Normally the time required for the active stage of composting of municipal waste by the windrow method is 2 to 6 months. A period of 18 months for bags to "degrade" would therefore require a considerable post-composting curing period to allow this to occur.

Testing of Degradable Plastics

In addition to the need for agreement on definitions of "photodegradable" and "biodegradable" plastics the literature search revealed that there is a need for standardization of test environments and test methods if the performance of degradable plastics is to be assessed more fully. At the present time ASTM Subcommittee D20-96 on Environmentally Degradable Plastics is reviewing these needs and has started to address the standardization issues.

Test environments need to be characterized, be reproducible and relate to the intended purpose and fate of the degradable plastic material. Accelerated laboratory tests which show correlation to field environmental conditions would be preferable. Comparison with the behaviour of a well characterized "normal" plastic and with known biodegradable polymers such as polycaprolactone or cellulose under the conditions of the test environment may be one method of achieving this for evaluation of biodegradable plastics. The starting test materials also need to be well characterized before testing. Similar requirements would apply to plastics with photodegradable claims.

Standardization of test methods for measuring changes in physical and chemical properties during exposure and the rate at which these occur in the test environments are also required. These may range from simple measurement of weight loss as a measure of volatilization to on-line measurement of carbon dioxide and methane production using a biometer to measure rates of true biodegradation. There is also a need to quantify the end-point or end points of degradation if "degraded" is to be defined for photodegradable, biodegradable and photo-biodegradable plastics.

Further research to characterize the intermediate products and end products of plastics with enhanced degradation claims is required.

Possible toxic or adverse environmental effects of these degradation or partial degradation products also requires investigation.

Key Findings from the Literature

1) There are no universally accepted definitions of biodegradable or photodegradable plastics. The American Society for Testing Materials (ASTM) and the Canadian Standards Association (CSA) are addressing this issue.

2) There are currently no universally accepted standards or test methods for evaluating the performance of degradable plastics. ASTM and CSA are addressing these issues.

3) It is recognized that an accelerated loss of physical properties of plastics can be induced through the addition of certain additives. Conventional plastics also degrade although the time required is substantially longer. Consequently any reference to controlled lifetimes of degradable plastics is a relative rather than an absolute term.

4) There is agreement in the literature that unless polymers such as polyethylene are degraded to low molecular weight straight chain alkane fractions (molecular weight less than 1,000 average) little or no biodegradation can take place as evidenced by microbial plate growth tests or soil burial tests. Branching of the alkane chains appears to prevent biodegradation regardless of molecular weight. Most studies on biodegradability have been carried out on polyethylene and little data are available on other commodity plastics such as polystyrene.

5) There is very little information on the by-products or end-products resulting from degradation of either conventional plastics or plastics with enhanced degradation. The fate of these

degradation products is largely unknown. In addition, little is known about the potential effects of release of plastics additives, for example, organometallic antioxidants, on degradation of the packaging. As a result the environmental impact cannot be assessed at this time.

6) The effects of degradable plastics on the recyclability of plastics is unknown. Further study and research is required in this area.

1. INTRODUCTION

Plastics have come under increasing attack by the public as a major contributor to litter and to solid waste disposal problems. Although plastic waste currently in North America makes up only about 7% of municipal solid wastes on a weight basis it is highly visible since it constitutes about 18% of the initial volume of municipal waste (Thayer, A. 1989) and may take hundreds of years to degrade when discarded to the environment as litter or to landfill sites. The percentage of waste composed of plastics has also nearly doubled in the years 1976 to 1984 (General Accounting Office, U.S., 1988) and this has lead to mounting concerns about a potential crisis in plastics waste disposal.

The traditional methods for dealing with solid wastes such as landfilling or incineration encounter strong public opposition when new and needed solid waste facilities are proposed. The "not-in-my-backyard" (Nimby) syndrome is the prevailing public reaction when the creation of a new landfill site or incineration facility is proposed for a community. Environmental concerns such as contamination of groundwater or air pollution account for much of the public's reluctance to support locally these solid waste disposal options. As a result, other options which could reduce litter and extend the life of existing solid waste disposal facilities such as separation and recycling of wastes including plastic wastes and the use of degradable plastics have been proposed. Proponents of degradable plastics contend that the use of photo and/or biodegradable plastics is one way to help alleviate the problem while other experts believe that recycling of conventional plastics may be a more effective response to solving the environmental problems posed by plastics.

On superficial examination at least, it would appear that the use of degradable plastics which may deterioriate in months rather than the many years taken for conventional plastics would be an attractive option. Their use could reduce the life span of plastic litter and diminish the accumulation of plastics in landfills.

Recently, divergent views and legislative actions have been proposed by various environmental groups and government agencies to either ban degradable plastics or to mandate degradability for certain plastic materials. For example, in Italy a ban on the sale of non-degradable plastic bags by 1991 has been enacted. In the U.S.A. there is a proposal to extend the ban on non-degradable beverage six-pack rings, presently in place in eleven U.S. states, nationwide. The State of Oregon has proposed a bill to ban non-degradable plastic coffee containers, food service items, bags and six-pack rings, fishing supplies and plastic industrial containers.

Concern over mandatory degradability has been expressed by the Council on Plastics Packaging in the Environment (COPPE), the Society of the Plastics Industry of Canada (SPI), the Association of Plastics Manufacturers in Europe (APME), Pollution Probe Foundation and the Ministry of the Environment in Ontario. These concerns are mainly that degradability will prevent the advancement of plastics recycling; that there is inadequate evidence to show that degradables will break down as claimed and that the environmental and health aspects of the residues or partial breakdown products are largely unknown.

As a result of these uncertainties on the performance of degradable plastics and their potential to alleviate the plastics waste and litter problems, the Ontario Ministry of the Environment and the Environment and Plastics Institute of Canada requested a research proposal to study degradable plastics addressing the following areas of concern.

1) Are biodegradable plastic products and the residues of photodegradable plastics biodegradable with respect to time and process?

2) Will the presence in the waste stream of degradable plastic products affect the technology of recycling plastic waste and the quality of products produced from recycled resins?

3) Does the presence of degradable products provide benefit to the collection of waste and the efficient use of incineration and landfill as a means of disposal?

4) Does the introduction of degradable products change the attitude of the public to the generation of waste and litter?

The present study was commissioned by the Environment and Plastics Institute of Canada (EPIC) and the Ministry of the Environment of Ontario (MOE) to investigate the first and fourth areas of the above concerns as a first priority in determining whether "degradable plastics" degrade under conditions in Ontario.

2. SCOPE

Biodegradable Commodity Plastics

The first part of this report outlines the literature search strategy to obtain information on degradable plastics; definitions of degradability/ biodegradability and the findings from the trade, patent and refereed journal literature search on plastics with biodegradable claims. The claims and scientific findings for biodegradability of commodity plastics are reviewed and commented upon in the light of current methods of disposal to landfills and composting operations or by soil burial.

Photodegradable Plastics

The second section of this report examines in detail the history and current status of plastics which are claimed to possess enhanced photodegradability. It is noted that the key word here is "enhanced" since it is well known and accepted that all large volume usage commodity plastics are susceptible to varying degrees of photodegradation when exposed to sunlight. For example, even in a relatively low sunshine climate such as that of the United Kingdom, the Industry Council for Packaging and the Environment has noted that "...polyethylene, polypropylene and polystyrene, which make up some 90% of all plastics used in packaging, will usually reach a fragmentable condition in about two to three years with complete exposure to sunlight in the UK unless specially protected." (Read 1989).

It is well beyond the scope of this report to evaluate and comment upon the very large number of publications relating to not only the general mechanisms of photo or photo-oxidative degradation of plastics but also to the development and evaluation of additives designed to minimize or prevent such breakdown.

In the same sense, while there is no standardized definition of the word "enhanced", it is generally accepted that some modifications to plastics will render them susceptible to higher rates of chain breaking events. The scientific literature contains hundreds of publications relating to the Norrish Types I and II photoreactions in carbonyl containing substances, both polymeric and small molecule, alone. The interested reader is referred to a slightly dated but still excellent monograph by Ranby (Ranby et al. 1975). Again, a detailed review of these is not considered to be within the scope of the current report.

3. OBJECTIVE

The overall objective of the study is to determine if "degradable plastics" currently in the market in Ontario degrade under conditions in Ontario and Ontario landfills.

This report deals with Phase I of the investigation encompassing the following task:

- Review and critique of the literature on photodegradation and biodegradation of plastics and the adequacy of test procedures used to determine or forecast time and conditions to degrade in Ontario.

4. LITERATURE SEARCH

The literature search strategy for the "biodegradable" aspects of this report employed the following keywords: biodegrad*, plastic*, polymer*, polypropylene*, polyethylene*, polyolefin* and/or polystyrene*. The symbol "*" indicates that the word has been truncated to include any suffixes that may apply to the particular word. For example, biodegrad* would include biodegrades, biodegradable, biodegradation, biodegradability, etc., in the literature search. The keywords were searched singly and in combinations to obtain relevant references. The references from each database file were printed off-line, reviewed and pertinent papers were ordered. The following is a list of databases searched by on-line computer access by ORTECH International, using the key words and search strategy described above:

Agribusiness U.S.A.
Agricola
Analytical Abstracts
Aquatic Sciences and Fisheries Abstract
Biosis Previews
Biotechnology Abstracts
CA Search
Chemical Engineering Abstracts
Current Contents Search
Dissertation Abstracts On-line
Enviroline
Environmental Bibliography
Federal Research in Progress
Food Science and Technology Abstracts
Foods Adlibra
Materials Business File
NTIS (National Technical Information Service)

Packaging Science & Technology Abstracts
Pascal
Pollution Abstracts
PTS Promt
Scisearch
Supertech
Water Resources Abstracts

A second literature search was conducted for ORTECH by NERAC, a professional computerized literature search company associated with NASA. NERAC maintains on-line access to an array of U.S. and international databases. NERAC designed a search strategy entitled "Biodegradable Polymers". This literature search included a retrospective search, dating back to the early 1970s, as well as a current awareness search that automatically forwards any new references to us. The following is a list of databases searched by NERAC:

Biobusiness
Biological Abstracts
CA Search (Organic, Macro and Applied)
Chemical Engineering Abstracts
Conference Paper Index
Engineering Index
Federal Research in Progress
Food Science and Technology Abstracts
Inspec
Life Sciences Collection
Paper and Board Printing and Packaging
Predicasts - New Product Announcements

PROMT, Predicasts
Rubber and Plastics Research Abstracts
U.S. National Technical *Information Service*
U.S. Patents (Claims)

A description of each database searched is included in Appendix A. These descriptions detail the years of coverage, as well as indicating subject areas and sources of information available in each database file.

5. DEFINITION OF DEGRADABILITY

The term "degradable plastics" implies that "normal" plastics are non-degradable which is not the case since all polymers will eventually degrade in the environment although the process may take centuries to occur. However, because of their longevity, many would regard normal thermoplastic materials as "non-degradable" for all practical purposes.

The term "degradable" is generally used to identify a class of plastics which have been compounded or engineered to rapidly degrade in a relatively short period of time in the environment. These enhanced degradable systems presently fall into two groups - "photodegradable" and "biodegradable".

There is a need for a definition of degradability if the performance of "degradable" plastics is to be assessed. In legal terms, degradability will require clear and unequivocal definition if misunderstanding of claims on "degradation" are to be avoided, but it is difficult to construct a practical chemical definition to meet this need. The popular concept of "degradable" incorporates both chemical degradation of the polymer into shorter chains and the physical breakdown or deterioration of the plastic material into fragments.

A recently proposed definition for degradable plastics by the Terminology Section of ASTM Subcommittee D20.96 on Environmentally Degradable Plastics (ASTM 1989) incorporates both these aspects and would encompass both photodegradable and biodegradable plastics.

"Degradable Plastics: Plastic materials that undergo bond scission in the backbone of a polymer through chemical, biological and/or physical forces in the environment at a rate which is reasonably accelerated, as compared to a control, and which lead to fragmentation or disintegration of the plastics".

Both degradation and deterioration processes usually take place in the environment although the latter process may be much slower. Because degradation is a gradual and on-going process, determining at what point a waste degradable plastic material becomes environmentally acceptable is not an easy task. Loss of mechanical strength so that wildlife can escape unharmed from discarded plastic nets or rings, if they become entangled, may be sufficient for a concerned ecologist. The general public on the other hand may perceive environmental problems which will not be satisfied until plastic litter becomes embrittled and deteriorated to a particle size indistinguishable from dust. From a chemical or biochemical viewpoint however, accumulation of plastic "dust" or other degradation by-products could still be an environmental problem and may require that the polymer be further degraded to smaller molecules leading ultimately to carbon dioxide and water. The time scale for degradation of plastics with enhanced degradability may, therefore, vary from weeks to many years depending on the method of disposal to the environment and the perceived satisfactory end point of the degradation process (Andrady 1988).

In considering what constitutes satisfactory performance of degradable plastics the terms of reference regarding product type and application, mode of disposal, expected environmental conditions, time frame etc. should be specified in order to avoid any misunderstanding of claims for degradability. How to best ascertain the type and amount of degradation under these conditions (or simulated conditions) must then be determined. This would include residue testing to determine the "harmless" characteristics of intermediate or by-products produced from the plastic material during the stages of degradation.

Although a great deal of public debate and discussion has taken place recently including press releases and trade journal articles about the environmental concerns of plastics disposal and the pros and cons of degradable versus non-degradable plastics, little evidence on the performance (or lack of performance) and characteristics of degradable plastics has been documented in scientific journals. It is interesting to note that Guillet, commenting on public concerns on environmental matters in a preface to a book on "Polymers and Ecological Problems" published in 1973 said "... much of this public debate has been characterized more by ardour than by information, and often the wildest speculations are promulgated with the same appearance of veracity as hard scientific facts. It is an important, and often neglected, duty of scientific societies to make sure that the public is properly informed regarding the technical aspects of matters of public interest, and to assure that policy decisions of governmental and other agencies are made with due regard to the scientific and technical facts, so far as they are ascertainable". (Guillet, J. 1973a).

The intention of this report is to critique what has been published to date on the claimed or expected performance of commodity degradable plastics using as far as possible documented information published in scientific journals, the patent literature and independent or third party reports.

6. BIODEGRADABLE PLASTICS

There appear to be two types of biodegradable systems, one in which surface modified starch or gelatinized starch is incorporated along with an oxidizing agent such as a fatty acid or modified vegetable oil to act as an auto-oxidant and the other based on the use of a natural polymer or polymers such as polyhydroxybutyrate/valerate.

6.1 Starch Modified Systems

An example of the starch type additive system which is available as a commodity material is St. Lawrence Starch of Mississauga's "Ecostar" system. Plastics made with the Ecostar system incorporate a modified low moisture (<1%) starch treated with silane to make the normally hydrophilic surface of the starch hydrophobic. Several different starches such as cornstarch in granular sizes of 15 microns, rice starch (5 microns) or potato starch (80 microns) can be used although cornstarch is the most common. A fatty acid or other autoxidant is also added to the system. The common polymers in which masterbatch formulations can be used are said to be polyethylene, principally low density polyethylene (LDPE), or linear low density polyethylene (LLDPE), polypropylene (PP) and polystyrene (PS).

The underlying theory for enhanced biodegradability of Ecostar systems (Maddever W. and G.M. Chapman, 1989a and 1989b) is that degradation proceeds by two interactive mechanisms. The starch present as granules in the polymer is attacked by microorganisms until they are completely removed. This weakens the polymer matrix and increases the surface area of the plastic. The second mechanism results from the formation of peroxides by the auto-oxidant when it comes into contact with metal salts present in soil or water. The peroxides begin to break the polymer chain and this second mechanism is said to be enhanced by the increase in surface area brought about by the first mechanism. The breakdown of the polymer chain into units of lower molecular weight is said to not only weaken the material but to occur to a level where the polymer can then be metabolized by microorganisms to carbon dioxide and water.
The rate of degradation is said to depend greatly upon factors such as moisture, temperature, pH, presence and type of microorganisms, presence of metal salts, the relative proportions of polymer and additives, polymer type and the surface area and thickness of the article.

For many applications the authors state that definitive and rapid degradation times are not required and cite examples of products such as shopping bags, garbage bags and films used for hygienic products where product specifications and performance during use are demanding but the rate of degradation is non-specific. For applications such as plastic compost bags and mulch films more rapid degradability rates are required and St. Lawrence Starch has developed "Ecostar Plus" which is said to be similar to the Ecostar system but with accelerators added which are claimed to not only enhance biodegradability but also photodegradability for such applications.

The papers by Maddever and Chapman contain, in addition to the theory on mode of action, some information on methods which have been used for testing and data on deterioration with time as evidenced by loss of tensile strength.

The statement by the authors that definitive and rapid degradation times are not required for items such as garbage bags and shopping bags presents a very broad base for interpretation of satisfactory field performance for degradability and leads to controversy. Certainly one can agree with the authors that the environmental conditions in a landfill site are ill-defined. It would be difficult to predict rate of degradation of even fully biodegradable materials such as cellulose in most landfill sites. However, it would be reasonable to expect evidence of degradability under "ideal" or specified test conditions which might then relate to landfill conditions which were optimized for biological action to occur. Very little definitive information on biodegradability under defined conditions has been published in peer review journals. Information which is available has been released either in patent filings, in papers presented at conferences or in press release type articles by the companies. To some extent this is understandable because of protection of proprietary interests in what is perceived as a growing commercial market for degradable plastics. The companies involved also appear to be continuing to experiment with different compositions in attempts to improve or balance product performance with better defined degradability for certain niche markets e.g. bags for municipal composting programs. What little evidence of biodegradability of starch filled polymers is as follows:

6.1.1 Role of Starch in Starch Filled Polymers

Work by Griffin over a ten year period at Brunel University in England was presented in a paper at an International Conference on "Plastics 2001 a look at the Future" in 1984 in South Africa (Griffin, G.J.L. 1984). He reported that when starch filled films were immersed in starch digesting enzymes (amylases), under appropriate conditions that a substantial proportion, depending on the starch concentration, of the starch filler was digested. This permeability of thin polyethylene films to starch enzymes was surprising to the author since from SEM micrographs the starch granules appeared to be almost perfectly wrapped or encased in polyethylene. The phenomenon appeared to be a characteristic of polyethylene films of less than one micrometer thickness (Griffin G.J.L.and P.S. Nathan, 1976). For typical packaging film thickness of 50 micrometers thickness in which starch granules of 15 micrometers diameter are embedded he indicated that those granules near the surface would have the thinnest covering because of melt stretching that occurred in the film blowing process and would be rapidly attacked by enzymes from microorganisms. Those granules more deeply embedded in the film would be reached by a "stepping stone" approach since many of the random granules in the film would be separated by only one micrometer of polymer or less. Swelling and physical disruption of the polymer surface was claimed to take place. Corroborative photographic evidence for this has been shown by Maddever and Chapman (1989a and 1989b) in SEM micrographs of PE film containing 15% starch before and after 6 weeks exposure to fungi.

Details of the thickness of the film and exposure methodology were not given but exposure conditions used in ASTM methods G-21 or G-22 may have been followed since the authors mention these as general test methods in the text. The attack on the starch granules was also claimed by the authors to increase the surface area of the polymer as well as weaken the structure. While all of this evidence for attack of the starch granules in PE film has stemmed from in-house R & D it should not be very difficult to verify the hypothesis independently using various commercially available starch filled polymers of various thickness. Exposure to bacterial or fungal amylases or to attack by mixed cultures of fungi such as those used in ASTM G21 or G22 or Mil Std 510D using basal salts media and/or a mixed microflora from sewage sludge under aerobic and anaerobic conditions is suggested. Microscopy (SEM), porosimetry and tensile strength measurements before and after exposure could be used to determine the extent of degradation of the starch granules, the increase in surface area and decrease in film strength obtained under defined conditions. This would establish the major claimed biophysical effects for the incorporation of starch in promoting weakening and opening up of the starch filled matrix under conditions favourable to microbial attack.

6.1.2 Role of the Auto-oxidant

Early work by Griffin and others in composting trials and soil burial tests indicated the importance of auto-oxidisable oils as polymer chain breakers since they observed faster degradation of starch filled polyethylene in the presence of cooking fats. Signs of failure were evidenced by the visible appearance of numerous cracks and after about a twelve month period of soil burial mechanical disturbances of the soil were said to be sufficient to cause fragmentation of the film.

These observations lead to the incorporation of fatty acids e.g. as corn oil or other auto-oxidants to the system to facilitate breakdown of the polymer. In the presence of metal salts in the environment peroxide formation is said to occur from the auto-oxidant which can then begin to break the polymer chain.

Recently Griffin (Griffin G.J.L. 1988) in an international patent application on degradable plastics indicated that *"an examination of circumstances in which polymer types used by the packaging industry appear to be degraded has disclosed a high probability in each case that the process of degradation has proceeded in at least two stages, the first being chemical and resulting in a reduction of the molecular weight of some part of the polymer to a point at which the second, biological, stage can commence as an interaction between the microorganisms of the environment and the low molecular weight material that has appeared"*. He also states that *"the first, chemical stage of this degradation process can follow different mechanisms which can be broadly classified under two headings the first being photochemical oxidative chain scission, and the second chemical catalytic oxidative chain scission"*.

There appears to be a concensus of opinion backed by evidence from photo-biodegradable systems that oxidation, not biological attack is the rate controlling step in the "biodegradation" process. As far as direct chemical catalytic oxidation is concerned where an auto-oxidant in the form of an unsaturated ester such as corn oil has been added no published information appears to be available as to how effective this is in promoting degradation of the polymer in the presence of metal salts in the soil. Johnson (1988) citing a personal communication from St. Lawrence Starch Co. indicated that following soil burial, polyethylene film containing 15% starch decomposes in six months and one with 6% starch in three to five years.

Presumably these films contained corn oil in the masterbatch since St. Lawrence Starch Company Co. acquired the patent rights to the earlier Griffin patents which claimed the addition of an auto-oxidant would degrade the synthetic polymer if buried.

The claimed degradation on burial is probably an uncertain process in practice for a number of reasons. The presence of certain levels of stabilizer and anti-oxidant required for processing of the polymer would obviously have an effect on subsequent oxidation of the polymer by an auto-oxidant additive as would environmental factors such as presence of metal ions, temperature and pH.

This is probably a reasonable assumption since "new and improved" formulations such as Ecostar Plus now incorporate accelerators to hasten the process (Maddever, W. and G. Chapman 1989a and 1989b). Graphs showing changes in elongation percentage of original for LDPE with no additives, Ecostar (10% starch), Ecostar Plus (10% starch) and LDPE with a photodegradable additive were shown in these papers but unfortunately no experimental details were given. The patent application by Griffin (1988) also indicates the need for the incorporation of catalysts which will initiate the primary chemical oxidation stage at a point in time when the polymeric material is discarded to landfill or for composting. The inventor claims that by selecting types and concentrations of anti-oxidants and pro-oxidants adequate stability for the short duration of processing of the polymer can be accomplished without affecting the subsequent chemical oxidation at the end of the normal functional life of the product.

The patent application disclosure describes a number of compositions comprised of blends of a saturated polymer such as polyethylene, a less stable chemically unsaturated polymer or copolymer such as styrene/butadiene block copolymer or natural rubber, an antioxidant, such as Topanol, active over a limited period and a latent pro-oxidant in the form of an organic salt of a transition metal such as cobalt naphthenate. The polymer composition preferably also includes filler particles such as starch or other biodegradable natural material e.g. cellulose. The presence of the anti-oxidant and the pro-oxidant in the correct ratios are claimed to give rise to a period of induction before a sharp loss of physical strength occurs i.e. to give an effective working life to the product before breakdown occurs. The presence of natural rubber or styrene-butadiene elastomers are said to not only provide adequate levels of auto-oxidisable unsaturation but also improve some of the physical properties of the products. Typical proportions of the unsaturated polymer or copolymer are in the range of 2% to 15% by weight of the composition. Starch, where incorporated, is also preferably in the range 2% to 15% by weight of the composition. The inclusion of starch is said to accelerate the biological breakdown of the scission products arising from the chemical oxidation.

To demonstrate the effects of incorporation of the ingredients in the composition the inventor conducted soil burial tests on 50 micron thick LDPE films and compared percentage tensile strength retention (ASTM Method D882-64T) against time of burial in months in well drained soil. Graphs showing the mean of five test results and the mean deviation at each measurement period indicate that compositions made degradable following the teachings of the invention maintained their strength for an induction period of about 3 months followed by a rapid loss of strength such that samples buried for a longer period were too weak to process for testing.

Control samples of LDPE of the same thickness from the same base polymer but without elastomer and pro-degradant additives were virtually unchanged. The technique of plotting breaking energy against time of exposure to test conditions was also used and was said to have the advantage that it takes into account loss of tensile strength and the reduction of elongation at break which are commonly observed consequences of the oxidative process.

Percentage weight changes of compositions incubated at 70°C to simulate composting temperatures were also plotted against time. After an induction period, samples with catalyst and elastomer oxidized rapidly after five days. No data were presented on the biological action subsequent to oxidation or evidence of oxidation leading to scission of the polyethylene backbone although this could have occurred at the same time as oxidation of the unsaturated elastomer. Oxidation of the latter could have accounted for much of the loss of strength of the films with additives after soil burial or elevated temperature incubation.

The inventor appeared to be satisfied with fragmentation of film compositions as a satisfactory end point since he stated that *"...after a period of 6 to 12 months the materials would, as a result of their advanced degradation, be impossible to retrieve from a typical landfill mass without fragmentation"*. He further stated that *"small fragments of polymeric material are accepted as innocuous components of the soil in respect to the absence of any phytotoxic effects or interference with the quality of "drainage water"*. Presumably this latter statement was with reference to the use of material as degradable mulch film in agricultural practices.

If claims for biodegradability are to be made it would be desirable to show (a) that scission of the stable polymer (e.g. polyethylene) backbone does occur in such systems and (b) that the breakdown products resulting from chemical catalytic oxidation are capable of being assimilated and metabolized by microorganisms eventually to carbon dioxide and water. Evidence published to date only indicates that under certain conditions the polymer compositions will lose their integrity and fragment. Most of the recent commercial research and development appears to have been directed more towards development of systems with a built-in "package" of pro-oxidant(s) and oxidizable and/or biodegradable components which can more predictably result in deterioration and fragmentation of the polymeric product when discarded to landfill or composting operations. (Griffin 1988; Chiquet 1988; Otey et al. 1987).

6.2 Biodegradable Polyesters

Potts et al. (1973) found that only low melting and low molecular weight polyesters showed a reasonable degree of biodegradation. An example of a biodegradable polyester is polycaprolactone developed by Union Carbide and has been used to make an injection molded seed container for tree seedlings. The container which takes about a year to biodegrade in soil allows for planting and acts as a protective sheath. Although developed and tested in the 1970's the containers have proved too costly for commercial use.

Bailey and Gapud (1985) have demonstrated that introduction of 10% ester containing groups into the backbone of polyethylene renders the copolymer highly degradable. To date these copolymers of ethylene and 2-methylene-1, 3-dioxepane have not been commercialized (Gibbons, A. 1989) although the material is said to have the strength and flexibility of conventional polyethylene.

The natural biopolymer, polyhydroxybutyrate (PHB) and polyhydroxybutyrate/polyhydroxyvalerate copolymers (ICI BIOPOL) produced by the bacterial fermentation of sugars has the potential for providing a commodity biodegradable plastic. Biopol is a truly biodegradable thermoplastic since it is a material which a number of bacteria and fungi use for energy storage. Degradation of PHB and the PHB cycle has been described by Dawes (1988). The rate of degradation of Biopol is such that packaging films 50 microns thick are totally degraded in 1-2 weeks in anaerobic sewage, 7 weeks in aerobic sewage, 10 weeks in soil at 25°C and 50 weeks in sea water at 15°C (Uttley 1986). At the present time because of small pilot scale production and hence higher cost (U.S. $15/lb.) the material is mainly being used for small high value added products. Commercial scale plant production is expected to reduce this to U.S. $1/lb. (Leaversuch 1987).

7. BIODEGRADABILITY OF SYNTHETIC POLYMERS

From the literature review the following information on the biodegradability of synthetic polymers has been noted.

High molecular weight synthetic polymers containing a largely C-C backbone as a class are generally resistant to biodegradation. Exceptions are polymers with aliphatic esters in the main chain (e.g. ε-caprolactone polyester) (Potts et al. 1973) and polyurethanes based on polyester diols (Darby and Kaplan 1968; Potts et al. 1973). Additives to synthetic polymers such as some plasticizers have been shown to be biodegradable although the long polymer chains are not susceptible to attack (Klausmeier and Jones 1961). Lower molecular weight hydrocarbons are more susceptible to attack.

Potts et al. (1973) investigated the biodegradability of a large number of commercial plastics, in particular those used for packaging, and found that all of the large volume packaging plastics based on polyethylene, polystyrene and polyvinyl chloride were not susceptible to attack using ASTM Method D-1924 (as a fungal growth test) and soil burial tests. Samples where growth did occur showed no growth after the sample was extracted with solvent indicating that the original sample contained a biodegradable component and that the polymer itself is not attacked. These authors also investigated the effect of polymer molecular weight and branching. For linear hydrocarbon samples they found that samples with molecular weights up to about 450 (C_{32}) were susceptible to microbial attack. Above that point no growth was observed. Branched hydrocarbons of molecular weights less than 450 were not attacked.

They also pyrolyzed samples of low density polyethylene (LDPE), high-density polyethylene (HDPE) and polystyrene to obtain fractions of different molecular weights and tested these for degradation by fungi using ASTM Method D-1924-63. No growth was observed with polystyrene even with samples of an average molecular weight as low as 600 before pyrolysis and 4,000 after pyrolysis. HDPE supported significant growth up to an average molecular weight of about 3200 with trace growth still occurring at an average MW of 16,000. LDPE showed significant growth up to an average MW of 2,100 and trace growth to a MW 19,000. Pyrolyzed fractions would be expected to have a broad molecular weight distribution and to contain a proportion of short chain biodegradable molecules. It is therefore not surprising that some growth of fungi took place at an average of MW of 2000-3000 and light growth to MW of 16000-20000.

Karlsson (1988) in experiments with oligomers of polyethylene ($C_{28}H_{58}$, $C_{32}H_{66}$ and $C_{36}H_{74}$) also found degradation to be dependent on molecular weight. Where the oligomers were added to a nutrient solution inoculated with Chrysosporium, $C_{28}H_{58}$ and $C_{32}H_{36}$ oligomers lost 15% and 25% by weight respectively in four months while $C_{36}H_{74}$ lost only 0.2% by weight in the same period. Earlier work had shown a decrease in biodegradation for HDPE when films were extracted with solvent to remove most of the low molecular weight components (Albertsson 1977).

The Bioindustry Development Centre in a recent report entitled "General Situation of Degradable Plastics in Japan" (BIDEC 1989) presented a table showing the upper limit of molecular weight of hydrocarbon oligomers for biodegradability. The test method appeared to have used bacteria (rather than fungi) since degradation by Acinetobacter Pseudomonas, Nocardia and Moraxella species were reported. Again the upper limit for growth for ethylene oligomer was reported to be 600-800 and for styrene 200-300; butadiene 500 and isoprene 400 to 1000. There is therefore general agreement that unless the polymers are degraded to low molecular weight fractions (<1000 average MW) virtually no biodegradation can take place as evidenced by plate growth tests or soil burial.

Work at the University of Missouri in Columbia was recently presented by Tempesta (1989) at an ACS meeting in Dallas, Texas on a six month study with polyethylene film, with and without 6 percent starch, exposed to various environments. He reported that "starch is removed from the polyethylene under all environments" when exposed to conditions simulating a landfill, a compost heap, an anaerobic waste sludge digester and surface litter. Most rapid removal was under anaerobic waste treatment conditions and slowest in air.

He also reported that "the polyethylene degraded to smaller molecules" particularly under the anaerobic conditions where decomposition was greatest. It was reported that up to 15% of the 1200 carbon-long molecules gradually decayed into 25-carbon waxes.

If these observations under anaerobic conditions are confirmed some re-evaluation of conclusions based on earlier data obtained under aerobic or anoxic conditions may be required. No details of the anaerobic treatment environment have been obtained although operation was in the mesophilic range. A 5 to 10% change in polyethylene was said to occur in 6 months under these reducing conditions (Ianotti 1989).

Under extreme chemical oxidizing conditions using boiling nitric acid Mills and Eggins (1970) obtained waxy compounds from polyethylene on which thermophilic fungi could grow. Photo-degradation of polymers has also been shown to lead to a variety of physical and chemical changes including the formation of carbonyl groups. The photo-oxidation of polyolefins such as polyethylene and polypropylene have been shown to result in chain shortening and altered surface morphologies which contain ketone groups (Cicchetti O. 1970); (Carlsson D., D. Wiles 1969).

The biodegradability of ketones of increasing molecular weight was studied by Colin et al. (1976). They found that the growth rate for middle ketones decreased with increasing molecular weight although middle ketones up to C_{35} (MW>500) were still attacked and compared this to the work of Potts et al. (1973) on alkanes where chain lengths of up to about C_{32} (MW 451) were attacked. They also tested the biodegradability of UV irradiated LDPE and "Ecolyte" LDPE. The latter is a copolymer with ketone groups introduced adjacent to the main polymer chain to facilitate photo-oxidation of the copolymer.

The rate of photo-oxidation is a function of the number of carbonyl groups introduced. They found that highly irradiated LDPE supported negligible growth and the irradiated "Ecolyte" film supported only sparse fungal and bacterial growth. They postulated that the negative results with LDPE may have been because UV irradiation failed to produce a sufficient number of molecules of a chain length which were assimilable by microorganisms or alternatively that short chain molecules formed during irradiation are volatile and there is insufficient accumulation of susceptible molecules after irradiation to support growth. In support of this they noted that Blais et al. (1973) had observed that some short chain molecules formed during the UV irradiation of polyethylene terephthalate are volatile. Cornell et al. (1984) carried out more recent studies on the biodegradability of photooxidized polyalkylenes. The polymers they studied were commercial samples of polypropylene (PP), high density polyethylene (HDPE) and sensitized polyethylene (SPE). All were exposed to UV radiation under conditions which were at least qualitatively similar to those met in the environment i.e. freely circulating air and ambient conditions of temperature and humidity. The production of volatiles was determined by the loss of weight of exposed samples. All of the samples of film showed progressive weight loss with time exposure. The loss of weight by the PP samples was about 90% after 500 hrs of exposure to a 550 w quartz mercury lamp in air, while HDPE and SPE lost approximately 30% and 40% respectively in the same period. The authors surmised that the volatiles from HDPE consist largely of low molecular weight fragments and that most of the linear volatile products from PE and SPE would be ultimately degraded by environmental factors in the biosphere if they were linear hydrocarbons with a molecular weight less than 500. They also indicated volatile products from PP should contain highly branched hydrocarbon molecules and that these brached chain hydrocarbons may not be biodegraded since Potts et al. (1973) has shown that branched chains with molecular weights as low as 200 will not support growth.

The authors examined the oligomers formed by photodegradation of the polymers. This was carried out by solvent extraction at room temperature. In the case of SPE the oligomer fraction rose from an initial value of 5% in the unirradiated polymer to a limiting value of about 10% (concurrent with a marked and increasing rise in volatile production) after exposure to a quartz mercury arc in air.

The authors suggest that the data they obtained indicate that SPE undergoes an initial rapid photodecomposition and cleavage which results in a large reduction in the average molecular weight and loss of mechanical strength. As a result of this process a soluble oligomer fraction and a low molecular weight volatile fraction are formed. Continued irradiation appears to result in a steady state situation where as much of the oligomer is cleaved and volatilized as it is formed.

At the same time as loss of volatiles an increase in the concentration of cross-linked fraction was observed in the high polymer i.e. photolytic cleavage occurred with simultaneous formation of a cross-linked fraction. The fractions obtained by extraction of the polymer films as well as the extracted films themselves which had been exposed for various periods were also evaluated for their ability to support fungal growth using a modified ASTM G21 method incorporating spores of Aspergillus versicolor and Aspergillus flavus.. Tests were carried out at 30°C for 8 weeks. A further test using Cladosporium resinae a common hydrocarbon fuel-utilizing fungus was also used for evaluation. Only minimal growth was obtained with the insoluble high polymer fraction. The oligomer fraction obtained by solvent extraction of the photolyzed and the non-irradiated polyolefins is susceptible to microbial attack. Maximum growth was obtained on the first extract and each successive fraction gave oligomers supporting less profuse growth.

In their summary of this comprehensive study on photooxidation and biodegradation the authors mention the following points:

- There is no evidence that the high polymer itself will undergo progressive attack by microorganisms as a result of any mechanical dispersion on a supramolecular level.

- The primary non-volatile products of polymer photolysis are crosslinked polymer and oligomer. Lengthy irradiation of SPE resulted in a crosslinked fraction comprising about 30% of the polymer residual. This residue did not support microbial growth and because of the crosslinking would be relatively recalcitrant to degradation by environmental agents, physical or biological.

- The common types of polyolefins contain small amounts of oligomer (the amounts depending on manufacturing and processing conditions) which give evidence of minimal microbial growth *in situ* when the intact polymer is challenged. This confirms the earlier observations of Potts et al. (1973).

- If the oligomer is separated and challenged as a separate fraction it supports microbial growth.

- UV irradiation of the polymer will increase the amount of oligomer fraction, but probably not in excess of a limiting value determined by kinetic factors involved in oligomer formation and degradation.

- The results suggest that it is the oligomer fraction of the photolyzed olefins that is susceptible to challenge by microorganisms. (This is similar to observations and conclusions reached by Gilead and Scott (1982) and Scott (1988) that it is the oxygenated species formed during photo-oxidation which are biodegradable).

- Mechanical abrasion of light sensitive polyolefins that have been embrittled by exposure to UV radiation produces a fine polymer powder. In this form the polymer has a greatly increased surface area and can come in contact with soil and water microorganisms and their extra-cellular enzymes. It has been claimed by some authors that the finely divided polymers undergo enhanced and progressive microbiological attack (Guillet J.E. el al. 1974). The present results suggest that the appearance of enhanced growth in the finely divided polymer may be due to more rapid diffusion of the oligomer to particle surfaces.

They concluded that *"it does not appear then that residues from the degradation of polyalkylenes would be completely eliminated from the biosphere even by prolonged exposure to environmental agents including microorganisms."*

This paper by Cornell et al. at the U.S. Natick Laboratories helps to explain many of the observations and claims which have, and are being made, particularly with regard to photo-biodegradability.

7.1 Biodegradability Studies With ^{14}C Labelled Polymers

In order to study biodegradation in environments where degradation rates are very low, sensitive testing techniques are required. ^{14}C-labelled polymers have been used by a number of workers for such environmental studies over periods of weeks to as long as 10 years. (Guillet J. et al. 1974), (Albertsson A.C. and Ranby 1975), (Tsuchii, A. et al. 1977), (Albertsson A.C. et al 1978), (Kaplan D.L. et al. 1979), (Albertsson A.C. et al. 1987), (Karlsson, S. 1988).

Guillet J. et al. (1974) showed that polystyrene (PS) was virtually non-biodegradable and UV photolyzed Ecolyte PS (5% vinyl ketone) showed less than 1% of the radiocarbon as $^{14}CO_2$ in an 8 week study in soils and sewage sludge. Similarly, Kaplan et al. (1979) found extremely low decomposition rates for PS in a variety of mixed microbial communities including sludges, manures, soils, garbage and decaying plastics over periods of 5 to 11 weeks and that the addition of cellulose and minerals failed to increase decomposition significantly.

Albertsson et al. (1978) using ^{14}C labelled anti-oxidant-free high density polyethylene in abiotic and biotic environments in a study conducted over two years found that there was a slow abiotic "aging" at 20°C in the dark with some ^{14}C to $^{14}CO_2$ conversion. This was possibly due to oxidative autocatalytic degradation of the HPDE. They also demonstrated that pure anti-oxidant free HDPE solid product will not be attacked enzymatically by soil microorganisms in a direct way. Only the "extractable" low molecular fraction of the polymer seemed to be attacked giving rise to slightly increased (0.56% by weight) recovery of $^{14}CO_2$ compared to about 0.1% by weight for the abiotic controls over a period of 800 days.

In a series of papers Albertsson, Andersson and Karlsson (1987), Karlsson, Ljungquist and Albertsson (1988) and Albertsson and Karlsson

(1988) have presented the results of a 10 year study on ^{14}C labelled low density polyethylene films, with and without UV sensitizer added, which had been exposed to UV radiation for periods of 0,7,24,26 and 42 days before being mixed with water and soil or studied in an abiotic environment.

Their studies indicated that degradation initially was the result of UV light and/or oxidizing agents and that the carbonyl index increased with prolonged incubation in an abiotic environment. UV degraded samples in contact with soil showed, after an initial increase to a certain limit, a decrease of carbonyl groups with time indicating that when carbonyl groups are produced these are attacked by microorganisms. During the ten year period mixed with soil the study showed that LDPE which had been irradiated for 42 days prior to soil burial evolved 1.3 to 5.7% by weight as CO_2 and UV sensitized LDPE 3.5 to 8.4%. Samples of LDPE and UV sensitized LDPE under the same conditions which had not been irradiated evolved 0.2% and 1.0% by weight of CO_2 respectively. These studies disclose relatively low rates of "biodegradation" in soil with less than 10% biodegradation of UV exposed/UV sensitized PE in 10 years even though the final level of degradation appeared to be close to a decomposed structure. It also may be concluded from these studies that unless the molecular weight of the polymer is reduced significantly by photo-oxidation or by other physico-chemical oxidation mechanisms little "biodegradation" as evidenced by $^{14}CO_2$ production takes place. The experimental conditions mentioned by Albertsson, Karlsson and co-workers in soil were reported to be aerobic (10 mL/min) and maintained at a relative humidity of 40% by periodically adding water. (Albertsson A-C and S. Karlsson 1988).

If the authors mean moisture content of the soil was 40% then this would be sufficient moisture for biological growth to take place. At 40% relative humidity, conditions would be far below the optimum of 80-95% relative humidity (Rh) required for biological growth.

The authors did note with some samples "an increase in the degradation rate after each addition of water" which leads one to suspect that the experimental conditions in soil were at times less than optimum with regard to moisture conditions for good biological growth to occur. This may also explain why a somewhat higher rate for the biodegradation of ^{14}C labelled PE was observed by Corbin (1981) in soil where a conversion of about 2% per year to $^{14}CO_2$ took place.

7.2 FIELD STUDIES

7.2.1 Landfill Sites

No long term field studies with the specific purpose of studying the degradation and fate of plastics in landfill sites were revealed in the literature search. This is not surprising because of cost factors involved and the difficulty of conducting systematic studies with control over the various environmental factors which could affect degradation. There are some indirect studies which record observations on plastics recovered from ten and twenty year old landfills (Kinman et al. 1985, Kinman et al. 1989) which give glimpses of what may occur.

The 1985 report by Kinman et al. covers the termination of a 10 year pilot scale sanitary landfill co-disposal project at the US EPA Centre Hill Solid and Hazardous Waste Research Facility in Cincinnati, Ohio. Nineteen simulated sanitary landfills in the form of six foot diameter and twelve foot high lysimeters were used. These were watertight and gastight cells with leachate drainage, fitted with water input connections and gas and temperature probes.

Cells were loaded and packed into the lysimeters with garbage (approx. 7% of the composite was plastic/rubber/leather) in its "arrival at landfill condition". No attempt was made to break up large items or break open any sealed bags. Sludges and industrial wastes were layered on top of each lift in proportionate amount. The purpose of this study was to evaluate the physical, chemical and microbial condition of the nineteen simulated landfills at the completion of the 10 year co-disposal project. From their studies they reached a number of conclusions including:

- Industrial sludges did not prevent biological decomposition.
- Fecal matter was protected by plastic diapers and plastic bags.
- There was no channeling of infiltration water through the cell except when water was forced around large impervious items such as automobile tires, bricks or bagged refuse.
- Plastic bags protected food wastes and other readily biodegradable materials from decomposition.
- Paper bags protected food wastes and other readily biodegradable material from decomposition.
- Settlement of the refuse was unequal, since considerable material was protected from biological activity.
- Moisture content affected decomposition. Because of a leak one of the test cells where extraneous water seeped in had the greatest settlement and decomposition.

They also made recommendations including the following:

- Plastic and paper bags should be torn open as much as possible

to permit readily biodegradable material to decompose. (This is also important for more even settlement of the landfill area. The usual method of using a bulldozer to perform this task is adequate if layers are kept shallow according to the authors).

- Sufficient amounts of water should be permitted in a sanitary landfill to maximize decomposition, as long as leachate quality is maintained at a level which can either be recycled back to the landfill or treated for discharge.

- A study should be carried out to compare bagged refuse degradation versus unbagged degradation.

A second study by Kinman et al. (1989) reports waste composition analyses, physical/chemical analyses of the waste including moisture content, pH and alkalinity from a 17-20 year old landfill site closed in the late sixties and early seventies. General observations as to the degree of degradation and general appearance of the waste were made and specific analysis was also made as to plastics degradability. This was performed on all plastics by observing for signs of weakening discolouring, moisture, brittleness, microbial growth or other signs of degradation. Bomb calorimetry was used to quantify polyethylene plastics degradation. This was based on polyethylene having a heat of combustion of 18,000 BTU/lb at a minimum in its virgin state. Percent degradation was expressed as

$$100 - \left(\frac{\text{BTU of sample in BTU/lb}}{\text{18,000 BTU/lb virgin PE}} \times 100\right)$$

Important findings were as follows:

- For the majority of the carbon containing materials such as paper, wood, plastic, textiles which could serve as food for microorganisms biological degradation had occurred but at a relatively slow rate over a 20 year period, even though the moisture content of 14 of the nineteen samples examined exceeded 30%. All of these items were easily identified in the waste samples.

- All samples contained plastics (5.6% by weight on average) with signs of apparent degradation. Polyethylene garbage bags varied in condition from like brand new to considerable weakening and visible evidence of deterioration with holes, change in thickness, permanent stains through the material and cracking from loss of tensile strength.

- Twenty-eight of thirty polyethylene samples (93%) tested by bomb calorimetry showed significant degradation. 30% of the samples tested had degraded by 10% or more. The degradation ranged from 0.19% to 54.28%.

They were of the opinion that from the measurable degradation (by BTU value) that, if conditions are right, plastics may be degraded within the landfill in a shorter period of time than previously thought. It should be noted that degradation expressed as percentage reduction in BTU value per lb. would measure oxidative changes but not loss of volatiles. The values found by this method may underestimate the degree of degradation.

7.2.2 Composting

Griffin (1976) reported on the degradation of polyethylene in a composting operation. LDPE packaging film recovered from a commercial "DANO" horizontal cylinder composting unit after approx. 5 days at peak temperatures of 60-70°C, contained an average of 9% extractable hydrocarbon material. Using a laboratory size model of the DANO process the author showed that the peroxide content in the solvent extract of LDPE increased after composting. He suggested that there was a causal link between auto-oxidative peroxide generation in the unsaturated fatty acids of the liquids in compost and the subsequent degeneration of polyethylene. He also felt that composting garbage was, in general, a mildly agressive environment for plastics, much more so than garden soil.

Several studies have been undertaken on the use of biodegradable polyethylene bags for the collection of yard waste (mainly grass clippings) for composting. For example, in Lincoln, Nebraska, yard waste is being collected in polyethylene bags of 33 gallon capacity. The bags contain 6% cornstarch, a photodegradable chemical and a pro-oxidant which are said to make the bag more susceptible to oxidation and heat decomposition. The windrow method of composting is being used and the yard waste and bags are shredded and mixed with sewage sludge. Early results after 5 weeks of composting at 140°F (60°C) indicate that the bag material appeared to have lost strength and the original yellow colour had turned a brownish colour. Samples of the bags are being evaluated for loss of tensile strength by the University of Nebraska. It is estimated that the bags will degrade in 18 months (Hanlon G. and G. Brandt 1988).

8. TEST METHODS FOR EVALUATING BIODEGRADABILITY OF PLASTICS

If it is assumed that the test methods are to be used as the basis for evaluating or predicting performance in the environment e.g. landfill, composting, soil surface or burial then the conditions of the test should simulate as far as possible the conditions likely to be encountered in the environments. What conditions can typically be expected?

8.1 Environmental Factors - Landfill Site Conditions

In the case of landfill some thirty environmental variables that affect sanitary landfill degradation of municipal solid waste (Kinman, et al. 1989) have been identified. Factors such as moisture, temperature, types, numbers and physiological state of organisms present in the vicinity of the particle, degree of anaerobiosis, micronutrients, soluble metals are likely to be important for biological action to take place. Unfortunately, landfills in general act more as burial tombs than as bioreactors. Biodegradation of putrescible materials does take place to some extent as evidenced by methane production under the anaerobic conditions of landfill operations but this is far from optimal in most instances and continues at a slow and sometimes unpredictable rate for many years. Moisture is usually the chief limiting factor for biodegradation. Most landfills are designed to minimize water infiltration unless leachate control and recycle are practiced. Similarly the presence of inorganic nutrients, carbon sources etc. are likely to vary dramatically within the normal landfill site. All of this presents a rather difficult and unpredictable environment on which to base a test model for evaluating enhanced degradability of plastics in typical landfill sites. As has been pointed out by Johnson (1988) "biodegradation (of plastics) may have only marginal benefit since it (landfill) does not remove all materials or even biodegradable materials in a reasonable time".

8.2 Environmental Factors - Composting Conditions

In the case of composting there is a greater attempt to control the environment for biological decomposition. Moisture control, temperature and oxygen are the key monitoring and control parameters. In this aerobic decomposition process a moisture content of 50-60% of total weight initially is considered ideal, along with oxygen concentrations of 5 to 15%, pH of 6 to 8 and a temperature operating range of 55°C to 60°C. Particle size reduction is also important and a mix of large and small particles so as to maintain enough void space to allow air to circulate in the composting mass is desirable. Composting technologies can be classified into three general categories - windrow, aerated static piles and a variety of proprietary chamber or vessel systems such as drums, silos or bins and tunnels.

The simple windrow is a long triangular pile usually with a base of about 15 feet and a height of about 7 feet, the actual dimensions depending on the equipment used to turn the pile. The piles are turned about once per week with machines equipped with augers or tines, although front end loaders may also be used, to keep air supply and temperature within the pile at optimum levels. The time required for composting of municipal solid waste in windrows can be anywhere from two to six months. Windrow composting may also be used as a finishing or curing process in combination with chamber systems.

In aerated static piles the piles are placed over a network of perforated pipes coupled to an air-blower. The time for composting using this technology ranges from 6 to 12 weeks.

The chamber processes may be single or multi-chambered units which either rotate or can be mixed. The advantage of the vessel system is that environmental conditions can be controlled better and they can be operated in continuous or batch mode. Typical composting times for chamber processes are from less than 7 days to as much as 14 days. Most composting operations involve some post treatment including a curing period which may vary from weeks to months. Microbial action during curing will continue but at a slower rate than in the actual composting.

Depending on the system of composting used, a plastic material may therefore be required to degrade at a temperature of no more than 60°C in less than seven days to more than six months although this period could be considerably longer if the curing period is included.

8.3 Suggested Test Methods

In the case of landfill simulation it would be possible but very costly to use lysimeters within a landfill site and attempt to control the chief environmental factors governing the anaerobic decomposition of garbage. This would give some measure of the rate of degradation of enhanced degradable plastics versus normal plastics and biodegradable materials such as paper. Measurements of mechanical properties, weight loss, molecular weight and spectroscopic analysis of chemical changes could be monitored.

Accelerated testing in an anaerobic environment is suggested as an easier approach. The use of small anaerobic digesters operating in the mesophilic range (up to 40°C) with landfill leachate or sewage sludge is suggested. The rate of degradation could be monitored by gas evolution (CO_2 and CH_4), changes in mechanical properties, weight loss, molecular weight change and spectroscopic analyses of chemical changes with time.

Relative rate of degradation under these conditions could then be compared to identical reactors with "normal" plastics of similar type but without additives and to known biodegradable materials such as cellulose or degradable polymer such as polycaprolactone. By using an aqueous anaerobic system containing a mixed microflora of organisms together with an enriched nutrient supply in the form of municipal landfill leachate or municipal sewage sludge, environmental conditions should be at least as good as, or even better than, the most favourable environment likely to be encountered in a landfill. Only factors such as mechanical stress and thermal fluctuations present in landfill situations would be missing.

A minimum period of 6 months under anaerobic digester conditions would probably be required to assess whether there was a significant difference in degradation rate between plastic with additives for enhanced degradability and normal plastics. Differences in CO_2 or CH_4 production may be too small to measure by conventional methods if only slow biodegradation occurs. To detect small differences, labelled ^{14}C materials would have to be synthesized. Reliance may therefore have to be placed on measurement of changes in physical characteristics such as tensile strength, hardness, weight loss etc.

The method used by Kinman et al. (1989) where BTU measurements were made and the loss in BTU value expressed as percent degradation could be refined and perhaps used as a rapid method for the measurement of total oxidative changes taking place in the polymer when expressed on a weight basis. A measurement of overall loss may be possible by this method if measurements on a unit area basis can be compared to virgin starting material of the same thickness.

While there would be no way to directly relate the results from anaerobic digestion to a time to degrade in a landfill, a relative value relating to a biodegradable material such as cellulose or polycaprolactone and a very slowly degradable normal polymer would be obtained. Intermediate claims for enhanced degradability such as time to develop a porous structure (starch attack and removal), embrittlement etc. could also be evaluated using the test system.

To obtain data on the required time for polymers to degrade under aerobic composting conditions the use of a small laboratory composter patterned on the DANO composting process described by Griffin (1976) would provide a reasonable facsimile of a commercial process. If the enhanced degradability of the polymer in composting operations is based on the use of pro-oxidants it should also be possible to use a simpler environmental chamber procedure at a temperature of 55-60°C with high humidity and an atmosphere of 5 to 15% oxygen. This would not provide for microbial activity to take place but would allow a study of the rate and extent of oxidative changes and molecular weight reduction which are a prerequisite for biological attack to occur. Considerable changes in molecular weight would have to be observed within a time period of 7 to 14 days under these conditions for the polymer to be subject to biological attack in a commercial composting operation.

Testing in a soil environment would be required for photodegradable plastics which are designed or claimed to subsequently biodegrade in soil e.g. photodegradable mulch films. Soil burial tests, subsequent to UV exposure may be carried out with measurement of weight loss and tensile strength with time. Seal and Pantke (1988) have described petri plate growth techniques using a mixed fungal inoculum and soil burial tests. Fifteen laboratories in Europe participated in evaluating two polyurethanes - a polyester and a polyether type and a plasticized PVC using the petri plate technique. Twelve laboratories participated in the soil burial test. While these tests have been devised by the Plastics Group within the International Biodeterioration Research Group as standard tests for the resistance of plastics to microbial attack they could also be used for determining biodeterioration. They found that the petri plate technique with 28 days incubation at 28°C ± 1°C was not sufficient to clearly demonstrate the susceptibility of the polyurethanes to attack and it was necessary to extend the four week test period to obtain reliable data on weight changes. The weight loss in soil burial experiments for microbially resistant polyether polyurethane was on average 0.6% in six months and 0.9% in 18 months. For the microbiologically susceptible polyester polyurethane weight loss average was 2% after 6 months and 5.6% after 18 months. PVC lost an average of 15.5% in weight in 6 months and approximately 20% after 18 months. A similar pattern of sensitivity to biological attack was observed in tensile strength measurements. The results of these interlaboratory tests on microbially susceptible (PVC and polyester polyurethane) and resistant (polyester polyurethane) polymers were relatively uniform and statistically supported.

Similar tests could be adapted and used for the evaluation of polyolefin polymers with claims for enhanced degradability. While degradability as evidenced by weight loss and tensile strength measurements would relate only to the test environment a comparison could be made with the data of Seal and Pantke and to a normal unmodified polyolefin of the same type as the test sample.

9. PRODUCTS OF BREAKDOWN OF PLASTICS WITH ENHANCED DEGRADABILITY

Concern has been expressed that the degradation products of degradable plastics may constitute a pollution problem. The literature search did not reveal any studies which had been specifically designed to look at this potential problem.

The factors responsible for the environmental degradation of polymers in general are mainly thermo, thermo-oxidative, photo, photo-oxidative, chemical, hydrolytic and biological degradation. Depending on the environment, one or more of these factors may predominate. For example, plastic litter is likely to be subject mainly to photo, photo-oxidative and thermal effects. Degradable bags in a compost pile would be subject mainly to thermal and, thermo-oxidative effects although mechanical, hydrolytic, chemical and biological effects would also probably play a part.

These factors are likely to lead to the following degradation processes: Random chain scission, depolymerization, cross-linking, side group elimination or substitution, reactions of side groups among themselves.

These basic types of degradation processes seldom take place separately and the simultaneous application of various damaging factors, which is likely in the environment, makes evaluation of the degradation process very difficult. As a result the degradation products of degradable polymers are not well characterized, so their toxicity and environmental effects are unknown at this time. It should be noted that these degradation processes are likely to lead to similar end products for "normal" polymers and for polymers with enhanced degradability of the same type as far as the degradation of the polymer itself is concerned.

The rate at which products of degradation are produced is, of course, likely to be greater with enhanced systems. Other products which might be leached or be released on breakdown of the polymer are metals, anti-oxidants, pro-oxidant or activator residues, UV stabilizers and heat stabilizers. There is also loss of volatiles formed during breakdown and some of these may be branched short chain hydrocarbons resistant to biological attack.

Transition metals such as nickel and cobalt may be present originally as dithiocarbamate salts for anti-oxidant and light stabilizing purposes. Copper and iron from compounds used as light sensitizers are also likely to be found. None of these metals, metal salts or metal chelates would be expected to pose much of a problem if released since concentrations are small compared to other sources in, for example, a landfill site.

In general, additives of low molecular weight usually contain reactive groups and are much more sensitive to microbial attack than polymer molecules. It has been shown, for example, that heat stabilizers such as dibutyl tin dilaurate and zinc stearate (lubricant) readily support growth in ASTM fungal growth tests. (Kelen 1983).

If the polymer itself is photodegraded (see Sections 10.3 and 11.2 for futher discussion on Photodegradation Byproducts and Toxicity), microbial attack will occur if the polymer is degraded to a sufficiently low molecular weight. However, it is likely that there will be an accumulation of plastic debris, particularly during photodegradation or thermal degradation in the form of a powdery material or plastic "dust". This material consisting of tiny fragments of the original polymer plus partially degraded and even cross linked polymer will probably have some carboxylic acid, ketone or alcohol end groupings. Whether this material becomes a polluting contaminant has not been established and will depend on environmental factors. For example, shredded or powdered plastic materials have been used to advantage as soil amenders in potting soils for plants. However, if similar powdered material is leached through soil into ground water as say the metal salt of a long chain carboxylic acid then this could be a ground water pollutant. No information on the characterization and fate of partially degraded powdered polymeric materials appears to have been published in refereed journals.

10. PHOTODEGRADABLE PLASTICS - HISTORICAL REVIEW

The coverage of developments in photodegradable plastics as relayed by industry journals, magazines and newspapers has seen considerable changes in emphasis since the early 1970's. Initial reports tended to be quite uncritical, for the most part simply accepting the manufacturers' or inventors' claims at face value. The main issues were performance related involving whether the materials worked as claimed and what added costs were entailed in their use. Very few challenges were made about assertions regarding, for example, the nature of the ultimate byproducts of the degradation processes themselves.

By the late 1970's this had clearly changed. An increasing number of articles began to address environmental concerns. Were the plastics ultimately only reducible to microscopic dust, thereby remaining in the environment though invisible? What byproducts were generated during degradation and were they potentially more hazardous than the original plastic article itself? Would the degraded material when sufficiently reduced in size by embrittlement and subsequent fracture be ingestible by wildlife? Would it migrate to the water table and transform a localized pollutant into a much more widespread one?

The debate began to achieve its present focus and magnitude by the early to mid-1980's. The passing of legislation by various governmental bodies mandating the use of photodegradable plastics in certain applications removed added cost of raw materials as an issue. This in turn sparked a large increase in the interest in the technologies available for meeting these requirements. At the same time the number of voices questioning the wisdom or the desirability of enhanced degradability or even whether the materials performed as claimed grew rapidly. Proponents of alternative technologies such as incineration and in particular, recycling have also become increasingly vocal.

This historical review has been structured with the intention of outlining the various claims being attached to photodegradable plastics. In a following section, the patent and peer reviewed scientific literature will be discussed to evaluate what independently derived scientific data exists to substantiate these. The primary claims which have been identified and which will be discussed in turn are:

- Photodegradable plastics present an attractive solution to the problem of plastic waste, particularly that in the form of litter.
- The ultimate byproducts of photodegradable plastics are carbon dioxide and water as a result of bacterial action.
- Degradation leads to non-toxic byproducts.
- Degradation rates can be highly controlled to match particular requirements.
- The materials are inert under ambient indoor lighting and only begin to degrade when exposed to sunlight.
- Photodegradables have no significant impact upon the recyclability of the plastics.

10.1 Environmental Attractiveness

One of the earliest references uncovered here (Anonymous 1971a) suggests that " photo-accelerating the degradation of polymers might well solve the disposal problem inherent in nonbiodegradable products". This was soon followed up with "Ecological concern, to eliminate littering and to dispose of solid wastes, has made attractive the concept of 'disappearing plastics' - plastics that would disintegrate after lying in sunlight..." (Anonymous 1972).The initial emphasis was, therefore, upon the visual pollution caused by plastic litter. This is further confirmed by J.E. Guillet who wrote " Here we are dealing with something which is not so much a pollution problem as a problem of aesthetics."(Guillet 1974). By the late 1970's the current form of the debate was beginning to emerge. Proponents of photodegradable plastics were strongly arguing that these were an effective solution to the problems of plastic litter. Others were claiming that since only a small fraction of plastics were ending up as litter and, therefore, outside of the recycling stream, it made little sense to mandate their large scale use even in only selected applications. Education and increased penalties for offenders were offered as more logical solutions. In addition, more recent concerns have been expressed as to whether the large scale advent of photodegradble plastics would actually encourage the public to increase their littering in the belief that "... a plastic hamburger tray or candy bar wrapper is just going to disappear..." (Woods 1989).

In conjunction with an increasing public awareness of environmental issues and an increasing political responsiveness to opinion polls outlining this trend, the effects of plastic litter on wildlife began to receive a higher profile in the trade literature. The harm done to marine creatures in particular was emphasized. By the mid-1980's, the aesthetic issues were strongly linked with harm to wildlife.Images of fish and waterfowl trapped by the plastic yokes from six pack beverage carriers became more familiar to the general public. This resulted in "Emotions run(ning) especially high against fishing nets, lobster pots and other plastics getting into marine environments" (Leaversuch 1987). The extent of the problem was described by "Plastics are responsible for the deaths of hundreds of thousands of sea birds and about 100,000 marine mammals each year. Much of the garbage causing these deaths is easily identified, and the problem could be reduced by making these products either bio- or photodegradable." (Cuthbert 1988).

More recently, some have expressed reservations about the claims pertaining to photodegradables as solutions to environmental problems. R. Leaversuch writes "Many in the plastics industry suspect (or insist) that the quest for plastics degradability is a fantasy driven more by political pressure than common sense." (Leaversuch 1987). Susan Mooney, an environmental scientist for the United States Environmental Protection

Agency states "We have questions about the performance of degradable plastics in the marine environment." (Wilder 1989) from the viewpoint that degraded plastics in the form of large fragments may themselves pose an ingestion threat to wildlife. The above illustrates that clear divisions of opinion regarding the attractiveness of photodegradable plastics as solutions to the problem of environmental pollution exist. The debate as carried on in the public forum is characterized by statements from both advocates and opponents of degradable plastics that are rarely, if ever, substantiated by independent studies or references to these.

10.2 Assimilation of Degradation Byproducts by Natural Organisms

Although there are a variety of approaches to enhancing the photodegradability of plastics, they all share the common objective of breaking long polymer chains down into shorter ones. The decrease in average chain length leads to a deterioration of the physical properties of the plastic. It becomes embrittled and subject to break up into smaller fragments as a result of natural forces such as rain or wind action. It is noted that in the absence of additives such as ultraviolet stabilizers and screening agents, most bulk commodity plastics are inherently photodegradable. The difference between "non-photodegradable" and photodegradable plastics lies primarily in the length of exposure time required to achieve this embrittled state.

As a result of ongoing photodegradation and natural mechanical forces, the plastic article or film continues to fragment into smaller pieces. Ultimately, the latter become invisible to the eye.

While this resolves the aesthetic issue of plastic litter, the question of what then becomes of the microfragments arises. In the early 1970's, it was generally assumed that soil bacteria would attack the microfragments, thereby further assimilating them into the environment. Statements such as "Polymers degraded by such means are converted to a sand-like powder that is believed to be readily broken down by bacteria." (Anonymous 1971a) typify this early optimism. To a casual reader it might well seem as though they simply vanish. However, invoking the Law of Conservation of Mass, L.L. Katan wrote on the subject of degradability that "It is a truism, often ignored and sometimes not known to the non-scientist, that...matter can not be destroyed." (Katan 1973).

The mechanism of photodegradation and the subsequent fate of the microfragments was further outlined by J.E. Guillet who was quoted as saying "When packaging made from this plastic is exposed to natural sunlight, it becomes brittle and reduces to granules which become part of the natural soil, susceptible to further biological decomposition. Eventually packaging plastics end up as carbon dioxide and water." (Anonymous 1973). Attaching some numbers from an unspecified source to this process, L.J. White wrote "... the polymer crumbles to a fine dust, and its molecular weight is reduced from about 80,000 to 40,000; as long as oxygen is present, the polymer will continue to degrade (even in the absence of light), reaching a molecular weight of around 5,000; and finally microorganisms take over to consume the remaining material." (White 1973).

The first questioning of this mechanism found during the current review appears in an article entitled "Degradable Plastics: Solution or Illusion?" (Taylor 1979).In it, L. Taylor refers to studies (Nykvist 1974) which indicate that "... the measured rate of biodegradation actually decreases with time; thus it seems that only the smaller molecular fragments are significantly biodegradable. Hence a measurable initial rate of biodegradation does not necessarily justify the conclusion that the material will be converted completely to water and carbon dioxide.".

By the mid to late 1980's, the trade literature was no longer reflecting the belief that the ultimate products of photodegradable plastics are carbon dioxide and water. Typical of many of the statements appearing in print is "Although litter from such a copolymer would not disappear, its susceptibility to fragmentation would make it less visible." (Sacharow 1987). More typical of recent trade literature articles are "Products that are made of degradable polymers eventually lose their identity, but they don't go away." (Erickson 1988) and "It's important to remember, however, that photodegradation merely breaks plastic down into tiny pieces. You haven't eliminated the plastic; it's just not as visible." (Kelly 1989).

In summary, the debate as carried out in the public forum has clearly moved away from the early contention that the ultimate byproducts of the photodegradation process are carbon dioxide and water. While breakdown of the articles to a plastic dust is generally accepted, blanket assertions as to the ultimate fate of the latter are no longer widespread.

10.3 Potential Toxicity of Photodegradation Byproducts

If complete conversion of the microfragments to carbon dioxide and water does not necessarily occur, the question arises as to what products are actually formed. In particular, the potential toxicity of these products is of concern.Further, for those photodegradables which depend upon sensitizing additives as opposed to polymerizable comonomers, the effects of additive release into the environment or package contents must also be taken into consideration.

An early article reporting upon the then new photodegradable plastic developed by G. Scott stated, with respect to the sensitizing additives, that "Though less is known about their toxicity, present information suggests they have none." (Anonymous 1971a). Referring to the Sty-Grade product from Bio-Degradable Plastics, a company spokesperson indicated that their sensitizing additive had United States Food and Drug Agency approval for uses with food and that "... the plastic degradation products exhibit no toxicity..." (Anonymous 1972). Similarly, in describing Ecolyte-S, a photodegradable polystyrene, it is stated that "The process does not introduce any toxic or potentially toxic materials..." (Anonymous 1973). The Journal of Commerce describes Plastigone, a photodegradable polyolefin as "Unlike ordinary plastic, which presents a major disposal problem after use, Plastigone is safe environmentally and dissolves completely into soil, leaving no residue." (Anonymous 1986a). The question of soil residues was further addressed by D. Gilead who claimed that no environmental problems are posed by the additives used by Plastopil of Israel (Anonymous 1988b). He is further quoted as saying "...toxic nickel used in some additives is present in such minute quantities that even after hundreds of years only negligible extra amounts would stay in the soil.". There is no reference made to what specific studies have been carried out to substantiate such claims.

In the absence of independently derived data, many have urged caution until more is known of the degradation mechanisms. Jeanne Wirka of the Environmental Action Foundation acknowledges end product safety claims by some industry officials but notes at the same time that no independent testing of the residues has been carried out. In the absence of such, she asserts that " It would not be good policy to make a national commitment to degradable plastics without first knowing their environmental impact." (Gibbons 1989). Perhaps the most comprehensive summation of these concerns has been made by L. Taylor who wrote "If we cause a polymer to undergo environmental degradation, we must consider the possible release of degradation products to the surrounding air, water, and/or land. In the case of polyethylene, such degradation products are probably environmentally acceptable; however, we should not assume that this will necessarily be true of all degradable compositions. Furthermore, degradation of a polymer may facilitate the release of additives (stabilizers, plasticizers, lubricants, etc.) which may be less inert than the polymer itself. When such additives are present in a nondegradable composition, the inertness of the polymer will inhibit their release to the environment. We must not assume that natural chemical processes, even biological ones, always produce products which are less toxic than the starting materials." (Taylor 1979).

This point of the debate then, appears to consist on one side of proponents of photodegradable plastics who generally claim that byproducts of the process are non-toxic or are sufficiently diluted in the environment that toxic levels are not ever approached. The other side consists of those who urge caution in the absence of independent verification of such claims. It might be of significance to note that not a single reference was uncovered in this review wherein claims were made that the byproducts are definitely toxic or harmful to the environment.

10.4 Controlled Lifetimes

One of the most frequently repeated claims made by the proponents of photodegradable plastics relates to the ability to produce materials having a "controllable" lifetime. It is noted at the outset here that at no time does any source define what is specifically meant by the term or under which exposure conditions it applies. The general approach has been to specify some time interval, ranging from days to years, and appending the modifying phrase "depending upon the amount of direct exposure to sunlight received". Seldom, if ever, is there any attempt to outline the large number of factors which affect the requisite direct exposure time available on a day to day basis. Descriptions such as "By varying the ratio of additive to polymer, a plastic can be granted a life of only a few days to as much as five years after direct exposure to natural light." (Anonymous 1971a) might leave a reader with the impression that additive levels are the sole determining factor in the plastic's lifetime. Since additive levels can obviously be controlled, this leads naturally to a similar status for lifetime.

The effective use of terminology by the proponents of photodegradable plastics likely has also, in large part, led to the general acceptance of the concept of controllability. For example, a phrase such as "... plastics that can be programmed to self-destruct..." (Anonymous 1973) through the use of the word "programmed" carries a powerful connotation of controllability.

As has been noted, very few demurrals regarding the notion of programmed, timed or controlled photodegradable plastics lifetime have been seen in the general literature. However, the failure of photodegradable mulching film to penetrate the British market has been ascribed to the "...variable and low intensity of the ultraviolet light ration in Britain which would stop the photodegradable film from degrading at a consistent rate..." (Read 1989). The author goes on to state "Indeed, this is one of the problems with photodegradable plastics - it is difficult to pin down how long the process of photodegradation will take."

The foregoing is not to suggest that controllable lifetimes cannot be achieved. In agricultural mulch applications in countries such as the southern United States or Israel, where daily hours of sunshine are relatively high and consistent, controllability becomes less an issue. However, in general such a claim must be firmly linked to a large number of factors other than simply hours of exposure. This would also be critical for the development of any set of standards which might be used to define any claims to photodegradability.

10.5 Stability Under Indoor Lighting Conditions

The key to the successful commercialization of photodegradable plastics, particularly in packaging applications, is found in the fact that these materials do not undergo breakdown under normal, ambient indoor lighting. Direct exposure to the shorter (290 nm to 330 nm) wavelength light of the spectrum of the solar radiation reaching the earth's surface is required to initiate degradation. However, recent developments in both indoor lighting and window materials technology might well become significant factors in the near future.

The sole reference to this question uncovered in the current review is contained in an article by P. Read (Read 1989). In it, the author writes "There could be problems with photcdegradable plastics, however, if they are used in an unsuitable indoor environment." She goes on to quote G. Griffin, one of the early researchers and developers of degradable plastics as pointing out that "... it was assumed early on that indoor exposure had no effect on these materials. And, as long as tungsten filament lighting was normal and very few buildings were fitted with Vita glass ultraviolet transmitting windows, this was a reasonable assumption.". Noting the rapidly growing use of quartz envelope high intensity lamps in store interior decoration, Griffin suggests that "Each material should be evaluated with these new circumstances in mind.".

Should newer lighting and window technologies combine to enhance the intensities of light in the shorter wavelength region discussed above, that are present under indoor conditions, claims as to the indoors stability of photodegradable packaging would need to be reassessed. In addition, any standards developed for such materials would clearly have to reference window materials and lighting sources.

10.6 Recyclability

Of the interest groups voicing concern over the advent of large scale use of degradable plastics, particularly in packaging applications, perhaps none have been quite so loudly heard as those advocating recycling as the technology of choice for the solution of the plastics waste problem. This issue is one which is characterized by both claims and counterclaims which tend to be general in scope and noticeably lacking in substantiation. In addition, it appears to be most often raised by those who are strongly opposed to or cautious about wholly accepting the new photodegradable technologies.

This imbalance reflects the current disparity in numbers between opponents and proponents of degradable plastics with the former also having greater resources available for publicizing their messages. The situation has been described by "At present, plastics-industry authorities who express either opposition to or doubts about degradable plastics have proponents severely outnumbered. And opponents include some heavy hitters indeed." (Erickson 1988).

It has been claimed that "Attempts to recycle plastic waste have not proven to be very successful, mainly because the sorting of the various types is nearly impossible." (Anonymous 1971b). Further difficulties have been ascribed to the normal growing pains of a newly emerging industry which is ". lacking the materials handling infrastructure needed to make the technology profitable." (East 1988). A lack of commitment on the side of the conventional plastics industry has also been suggested by Scott who, in reference to some practical solutions developed by himself and co-workers (Scott 1976) for some plastics recycling problems, wrote "Has the industry taken these to their breast as a solution to their problems? Not a bit of it! ... I haven't heard any outcry from the packaging industry that we as a nation appear to have given up the fight to control waste and litter." (Scott 1985).

Partially countering the latter point, J. Kelly notes that "To help recycling, The Society of the Plastics Industry developed a voluntary system of coding that identifies the package material." (Kelly 1989). In addition, community recycling bylaws are rapidly growing in number and are providing a boost to this method of dealing with plastics wastes. As S. Woods wrote "... collection systems, such as Ontario's Blue Box program, are being put in place and being well accepted by consumers." (Woods 1989).

Opponents of degradable plastics commonly argue that "... scrap generated during the manufacture of degradable products will tend to be

less suitable for re-use ... particularly if outdoor applications for the recycled material are contemplated." (Taylor 1979). In a similar vein, M Crawford writes "There are doubts about the real utility for degradable plastics, and some researchers are voicing concern that growing use of these materials could pose problems for emerging plastics recycling operations." (Crawford 1988). The proponents of photodegradable plastics argue that their comonomers or sensitizing additives have no effect upon the potential recyclability of their materials. J. Angus of Eco Corporation , a manufacturer of photodegradable plastics suggests that "If Ecolyte is present in a recycling stream, the degradation process can be stopped simply by adding antioxidant. This existing technology is commonly used by processors to recycle their own scrap." (Woods 1989). A. Redpath of Ecoplastics Ltd. (a subsidiary of Eco Corporation), in the same article, goes on to state that "Photodegradable plastics need not hamper recycling efforts. The dilution of recycled material with virgin resin will significantly increase the exposure lifetime of the blended resin. Most products made from recycled resins are either not exposed to sunlight or are sufficiently massive that degradability induced by a fraction of Ecolyte entering the recycle stream is not a practical concern.". Despite such assurances from photodegradable plastics proponents, many people remain unconvinced that recycling schemes would remain unaffected. Reflecting this caution, Collin Isaacs of Pollution Probe has been quoted as being concerned that "It's bad enough that when you recycle plastics they have to be sorted by type. If they also had to be sorted according to whether they were photodegradable, the job would become horrendous." (Woods 1989). In the absence of a thorough independent study of this issue, it will likely become an increasingly larger part of the debate in the near future.

11. PATENTS AND SCIENTIFIC PUBLICATIONS ON PHOTODEGRADABLE PLASTICS

As has been seen above, the debate over photodegradable plastics as carried out in the trade literature is characterized in general by fairly broad claims and counterclaims. In very few cases are the opinions supported by reference to independently derived data. This is not to fault the trade literature in any way as its primary function is to broadly inform its readership on new developments in materials and technologies. However, it does lead to the requirement of reviewing additional sources of information which provide more details on test methods used and specific results obtained.

While the manufacturers, developers and suppliers of plastics which display enhanced photodegradability likely have considerable data as to the performance of their products, direct contact with these potential sources of information has been deliberately avoided here. Such reports might well be viewed by some as being inherently biased as marketing and promotional requirements could affect their contents. Rather, the focus here has been placed upon patent literature and reports appearing in scientific publications. In the former case, the initial application generally does get independently reviewed in order to assess both the novelty and the validity of the claims made therein. For the latter, most reputable scientific journals have an anonymous peer review process for articles submitted for publication. While it is recognized that neither procedure completely eliminates unjustifiable conclusions from being drawn, it was hoped that the occurrence of such would be at least minimized.

As was stated in the scope section of the review, it is well beyond the scope of the current effort to comment upon the very large number of publications relating to the general mechanisms of both photodegradation and photo-oxidative degradationn of polymers. This has been a field of intense academic research for many years and is reflected in the number of published papers in the scientific literature. The emphasis here has been to focus upon those articles declaring a direct interest in the application of photodegradables in either packaging or agricultural mulching end uses.

Similarly, there is a large body of patents relating to enhanced photodegradability and particularly for polyolefin polymers. Claims numbering in the several of hundreds have been made for approaches for achieving this, entailing chemical modification of the preformed polymers, the use of reactive monomers in the production of copolymers, or the compounding of various small molecule sensitizers into the bulk polymers, or combinations of these three basic methods. The interested reader is directed to a review by L. Taylor which, though slightly dated, still provides one of the most comprehensive listings of the various approaches studied to achieve enhanced photodegradability (Taylor 1979).In view of this, the current review has generally focussed upon those methods which have found greatest commercial interest and actual development. In reading the applicable literature, information or data pertaining to the following factors had particular emphasis placed upon it:

- Definition(s) of photodegradability.
- Nature of intermediate and final byproducts of the degradation process.

- Environmental factors affecting photodegradation, e.g. humidity, temperature, surface and groundwater, sea water, UV wavelength (solar) and the time of exposure.

- Exposure test methodology.

11.1 Definition(s) of Photodegradability

In a recent United States General Accounting Office report to United States Senator John Glenn, it was stated that "We found widespread concern among officials and scientists about the current lack of standards. Definitions of such basic terms as biodegradation and photodegradation have not yet been agreed upon, nor have uniform methods of testing been developed." (General Accounting Office, U.S., 1988). This succinctly describes the situation as found to exist in the current review as well. For example,at a seminar on solid waste management, one speaker concluded that "... the expressions `degradability', `biodegradability' and `photodegradability' are relatively meaningless and should be more precisely defined." (Anonymous 1989b).

The problem actually appears to lie in the distinction between photodegradation and enhanced photodegradation. As has already been noted here, most commodity plastics are inherently photodegradable and must be stabilized to prevent premature breakdown when used in outdoors applications. Some generic descriptions have been supplied by L. Taylor who wrote that "In plastics designed to be photodegradable, absorption of radiant energy by the polymer molecule, an additive, or an impurity leads to formation of an `excited state' molecule, which then initiates reactions leading to the rupture or cross-linking of polymer chains." (Taylor 1979).

While this is quite valid it suffers from the shortcoming that it is also perfectly applicable to degradation in plastics not designed to be photodegradable.

Typical of most attempts to distinguish between normal and enhanced degradation materials is "Hence the interest in plastics that are degradable - strictly speaking more easily or more quickly degradable." (Katan 1973). The vagueness inherent to the words "more easily or more quickly" permeates the entire literature surveyed here. Representative of the patent literature is "... effects of weather upon these substances is that of accelerating decomposition..." (Henry 1972) and "... enhance their degradation when exposed to sunlight ..." (Swanholm et al. 1977).

Other efforts at describing enhanced photodegradability in the patent literature have included the concept of controlled lifetimes. Examples are "... so as to render them photodegradable in a controllable way." (Guiffre et al. 1976) and in reference to mulching films, "... where it is desired that the lifetime of the film can be controlled very precisely." (Gilead et al. 1985). In general, controllability is used to describe a product which remains essentially unchanged during its useful lifetime but then subsequently undergoes rapid degradation. While this serves to partially clarify the distinction between "normal" and "photodegradable" plastics it is far removed from a definitive description of the latter.

The lack of a generally agreed upon definition which is necessary for the development of a standard regulating what is or is not a photodegradable plastic could be critical for a newly emerging industry. It is particularly so for one that is substantially driven by legislation mandating its use in certain applications the potential for inappropriate business practices which might meet the letter but not the spirit of the legislation cannot be ignored.

This has been best described by L.L. Katan who wrote "Finally, the most difficult aspect is one which has little to do with science but a good deal with human nature. Assuming that a plastic article can be made to degrade to a specified level (eg brittleness) in x standard days (using an arbitrary local definition of standard) by the incorporation of y% of additive or comonomer, how can one be assured that y% (and not a cheaper, lower, level) has been used? An end user wishing to attract kudos from the matter could label his containers `Degradable plastic... environmentally friendly...ecological...' etc, while using only 0.0001 y% additive. Whereas a consumer is fully conscious, and reacts in the marketplace, to plastics packaging which is the wrong colour because of inadequate pigmentation, or dirty because of inadequate anti-static concentration, or discoloured because of inadequate heat stabilisation or anti-oxidants etc, etc, he cannot and would not know whether the degradable claim was justified." (Katan 1973).

In addition, the lack of agreed upon definitions of exactly what photodegradable means in the context of this technology could easily lead to materials being labelled as such while never having been intended by the manufacturer to be so. This difficulty arises from a lack of a precise definition of exactly what is meant by the terms "accelerated" or "enhanced". For example, in a patent describing an example of the application of the Bio-Degradable Plastics Inc. technology (Swanholm et al. 1977), brown, low density polyethylene (LDPE) films containing 0.1% 4,4'-di-t-butylbenzophenone (DTBBP) and 0.5% iron stearate were exposed to the output of a GE sunlamp for 125 hours. The brown pigment consisted of a mixture of iron oxides. After exposure, the average molecular weight of the LDPE was found to have been reduced to 170 from its initial value of 10,000. However, a brown LDPE film containing no DTBBP or iron stearate and exposed as a control sample under identical conditions suffered a reduction of molecular weight from 10,000 to 2,800, a drop of about 70% of its initial value.

This would be much more than the molecular weight decrease experienced by a clear, properly stabilized LDPE film and is attributable to the increased UV absorbance due to the brown pigment in the sample.

The point of the foregoing is that if photodegradability is not defined beyond the terms "enhanced" or "accelerated", the situation as it currently exists, then there is no reason why the simple, brown pigmented LDPE containing no additional sensitizing additives could not be labelled as photodegradable. Green or brown garbage bags made with current "non-photodegradable" technology could easily be marketed as photodegradable products.Indeed, R.J. Barrett, Mobil Chemical's general manager for solid waste solutions has been quoted as "The standard plastic bag can make quite an environmental statement. It is already degradable in sunlight as well as recyclable." (Anonymous 1988c, Anonymous 1988e). In view of the current lack of definitions for enhanced photodegradability, one would be hard pressed to disagree with the position taken by R.J. Barrett.

11.2 Nature of Intermediate and Final Byproducts

The study of photochemical processes occurring in solid polymeric matrices is considerably more complex than analogous studies on small molecules in dilute solutions. Reasons for this are varied and many. The first difficulty lies simply in characterizing the starting material as most polymers exist as statistical mixtures of chains of varying lengths. Depending on the method of synthesis, these chains may in addition have varying numbers of smaller side chains branching out from them.

The measurable effect of an event, for example a bond breaking, will then depend largely upon whether it occurs in a small side chain or the main chain. In the latter case, bond breaking taking place near the centre of the main chain will have a larger effect upon material properties than will a similar event occurring near the ends of the chain. In addition, the composition of the polymer chains may vary considerably. For a copolymer, chains formed early in the polymerization process may have a significantly different ratio of comonomers than those formed much later in the reaction depending upon such things as the relative reactivity ratios of the monomers and monomer feed ratios. A subsequent gross chemical analysis of the unfractionated product, even using such relatively sophisticated techniques as nuclear magnetic resonance spectroscopy (NMR), will yield only averaged compositional data.

The bulk polymer matrix itself forms a complex reaction medium for chemical events taking place in it. Commodity plastics such as the polyolefins are often characterized by highly crystalline regions where the polymer chains exist in close packed arrangements surrounded by more highly amorphous regions wherein the chains are in a greater state of randomness with respect to their mutual orientation. Photochemical reactions which are dependent upon various types of molecular motion, whether rotations around backbone linkages or diffusion of molecular entities towards or away from each other will generally take place more easily in the amorphous domains. In addition, whether the polymer is above or below its glass transition temperature (defined roughly as that temperature at which a glassy polymer becomes rubbery due to the onset of large scale motion of the polymer chains) can also have a large effect upon which particular reactions take place.

Further complications may also arise from such events as secondary photoreactions of the lower molecular weight byproducts before these can diffuse to the surface of the bulk polymer and volatilize. For photodegradable plastics based upon sensitizing additives, the uniformity of the blending of the latter into the polymer matrix could affect the subsequent degradation. In addition, the presence of colouring agents such as inorganic or organic pigments would be expected to affect the degradation process and the type and relative distribution of byproducts formed.

These factors all contribute to the field of bulk polymer photochemistry being one of ongoing, intense activity. Systems such as poly(ethylene-co-carbon monoxide) which have been known for at least forty years are still being characterized as to their photodegradation mechanisms and degradation byproducts (Gooden et al. 1984). As recently as 1988, studies on the environmental photodegradation of normal (i.e., not sensitized for enhanced photodegradation) low density polyethylene were reported on in the scientific literature (Severini et al. 1988).

A great deal is understood about the general mechanisms of polymer photodegradation and photo-oxidation. The interested reader is referred to an excellent if slightly dated monograph by Ranby (Ranby et al. 1975) or to a shorter, more general review of the field also by Ranby (Ranby 1989). What is lacking is the broader knowledge of specifically what chemical entities are produced with what efficiencies. In particular, much more needs to be known of the intermediates formed which are sufficiently reduced in molecular weight to be no longer classifiable as high polymers but are not yet volatile at ambient temperatures.

In this respect, the patent literature is noticeably unspecific. Very few patents reviewed here make any attempt to identify the products of their respective degradation processes. One of the few generic descriptions found here was in an Akerlund & Rausing patent relating to the use of substituted ferrocenes as sensitizers, which went as "Among the degradation products which are assumed to be formed in polyethylene under ultraviolet radiation in the presence of oxygen gas there are ketones, carboxylic acids, aldehydes, esters, peroxide compounds, unsaturations, ethers, alcohols, low molecular alkanes, water and carbon oxides." (AB Akerlund & Rausing 1972). It is perhaps interesting to note that the byproduct listing refers to normal polyethylene. Additional byproduct complexities resulting from the action of the photosensitizers are uncommented upon. One area of byproduct analysis has received a considerable amount of attention and this is the question of the ultimate biodegradability of the photodegraded plastic. The debate over this as carried out in the trade literature has already been discussed at length in the current review.

One of the earliest claims of proof of biological attack upon the fragments or "plastic dust" formed by the physical disintegration of photodegradable polymers following exposure to solar radiation appeared in a paper published by J. E. Guillet (Jones et al. 1974). Photodegraded Ecolyte polypropylene (EP) and Ecolyte polystyrene (PS) were studied along with a sample of low density polyethylene which had first been thermally degraded and then air oxidized to introduce carbonyl groups. The latter material,designated as EE, was expected to be similar in structure and molecular weight to the fragments produced by photodegradation of Ecolyte PE, a photodegradable polyethylene. It is noted that no evidence was offered of the validity of this assertion nor was it indicated why Ecolyte PE was not used in the first place.

The degraded products were mixed with garden soil, forest soil and land-fill soil in individual experiments and oxygen uptake rates due to

microbial activity were measured using Hach respirometers. Control experiments on the soils alone and containing non-degraded, non-photodegradable polystyrene powder were also run. In addition, studies of the biodegradability of these degraded materials in an aqueous environment were carried out using a medium comprised of sewage sludge. Oxygen uptakes were measured using Warburg flasks.

With the degraded EP and EP materials, the rates of oxygen uptake were in all cases clearly above the respective control rates. This was taken as clear evidence by the authors of the biological oxidation of the degradation fragments in the sewage sludge as well as in the three different types of soil used. The degraded PS showed no enhanced activity above the controls (including one having normal, undegraded polystyrene powder) and it was concluded that if biological activity was taking place, the experimental techniques being used were insufficiently sensitive to detect it. It was estimated, on the basis of the initial oxygen uptake rates, that complete biodegradation of the plastic would take place over a time period of about one year in natural soils.

Pursuing the polystyrene case further, J.E. Guillet and co-workers carried out a similar study using garden soil and activated sewage sludge containing photodegraded radioactively labelled styrene copolymers with vinyl ketone (Guillet et al 1974). Biological activity was monitored by trapping and measurement using scintillation counting, of the amounts of radioactively labelled carbon dioxide being produced.

Using this more sensitive technique, the authors were able to demonstrate higher rates of carbon monoxide production for media containing photodegraded polystyrene fragments as compared to control samples. In this case, however, the authors simply conclude that "... the fragments of polystyrene produced in the photooxidation of Ecolyte PS are more biodegradable than the undegraded plastic.". Noting that their data was limited, representing only the early stages of degradation, they decline to estimate the time required for total biodegradation.

In both these studies, plots showing biological activity, either as rates of oxygen uptake or formation of radioactively labelled carbon dioxide, display a tendency to level off at values of 10% or less of the theoretical totals based on initial weights of photodegraded plastics taken. For the case of Ecolyte PS in activated sewage sludge, this behaviour was attributed to a possible build-up of waste products of the bacterial colonies or to a depletion of the most readily accessible polymer fragments. The latter cause has been championed by others as will be discussed below.

While the foregoing studies are interesting, they might well have been even more so had additional information been supplied. For example, while the results of elemental analysis of the degraded polymers is given (Table II, Jones et al. 1974), corresponding data for the starting Ecolyte materials is not. Initial carbonyl contents are unknown. Similarly, while molecular weights of the degraded EP and EE polymers are given as being in the order of 2,200 to 2,300, initial molecular weights appear not to have been measured. Thus, it is impossible to judge the extent of degradation inflicted upon the samples. For the Ecolyte PS sample again only a final molecular weight of about 15,000 was reported.

The production of the EE sample by thermal degradation of low density polyethylene followed by air oxidation has already been noted above. The absence of analytical data to support the assertion of its equivalence with the photodegradation products of Ecolyte PE precludes an assessment of the validity of this claim.

It is also noted that the studies were carried out directly upon the Ecolyte masterbatch materials. Commercially, these are intended to be blended at levels ranging from about 10% to 20% with virgin, non-photodegradable resin to produce the useable plastic films or articles. The question, then, of what happens to this 80% or more of non-photodegradable resin is not addressed by these studies. Similar claims as to the ultimate biodegradability of the products of photodegradation of their materials were made in the patents describing the Bio-Degradable Plastics, Incorporated technology (Swanholm et al. 1975 and 1977). Following ASTM methods G-21-70 and G-22-67T which they describe as "qualitative in nature", the authors claimed to show that some fungi and bacteria were able to use the photodegraded fragments as a nutrient source. This entailed a modified plate count technique for determining the number of microorganisms present as a function of time.

It is of interest that the rates of microorganism growth on photodegraded, foamed polystyrene plastic as reported by Swanholm et al. are greatest within the first 14 days of the experiments and are greatly decreased during the subsequent 14 days (or within the first 72 hours of other tests lasting up to a total of 168 hours). This behaviour is qualitatively similar to that observed by Guillet et al. as outlined above and suggests either damage to the microorganisms occurs as a result of build-up of metabolic wastes or a depletion of the nutrient source. In the latter case, this would occur well before the majority of the photodegraded plastic was converted to carbon dioxide and water.

Omichi and Hagiwara described a technique for treating atactic polypropylene with gamma radiation under oxygen and/or chlorine gas atmospheres (Omichi et al. 1981). The modified polypropylene could then be blended with low density polyethylene to produce photodegradable films suitable for agricultural mulching purposes. Using films which had undergone accelerated aging in a xenon arc weather-o-meter, these authors evaluated the action of ninety two kinds of bacteria recovered from soils around petroleum wells on these potential nutrient sources. Over a three week test period, weight losses ranging from 8% to 18.7% of the photodegraded plastics were noted. Unfortunately, no weight loss data as a function of time was presented to allow an assessment of whether the biological activity was either constant or decreasing during the test period.

It is of interest to note that in the above sources, with one exception (Jones et al. 1974), no specific claims as to the complete biodegradability of the photodegraded plastics are made. Nor are there estimates given for the period of time required to achieve this. This contrasts sharply with the claims as made in the trade literature already discussed above. Others have studied this question of the biodegradability of the microfragments formed by the photodegradation of sensitized plastics and have reached conclusions which are perhaps not so optimistic as those outlined above. The basis for the contrary opinions was laid by some early studies carried out by J.E. Potts (Potts et al. 1973) wherein the ability of a variety of polymeric and small molecule analogues to support the growth of test fungi was evaluated. In summary, these authors found that while straight chain alkanes of molecular weights less than about 500 could support fungal growth, higher molecular weight materials could not. Branching of the alkane chains appeared to prevent their biodegradation by the fungi regardless of molecular weight.

Samples of high and low density polyethylenes of varying molecular weights were not able to support fungal growth except in those cases where average molecular weights were sufficiently low to ensure the presence of a significant amount of oligomeric species. This molecular weight dependence was attributed to both a decrease in the concentration of chain ends and possibly to their increased inaccessibility to the catalytic enzymes responsible for beta-oxidation as molecular weight increases.

In addition, Potts et al. studied the ability of polyethylenes degraded by pyrolysis to sustain fungal growth. Again, for both high and low density starting materials, it was found that molecular weights needed to be reduced to the order of 2,000 to 3,000 for growth to be observed. The authors conclude that "In both cases the attack is most likely on those molecules below 500 molecular weight that are present in the molecular weight distribution.". Finally, polystyrene as well as a large number of polystyrene and polyethylene copolymers with a variety of carbonyl containing comonomers were found not to support growth at all regardless of molecular weight or prior degradation by pyrolysis.These results are quite interesting in view of the data published by Jones et al. as already discussed here (Jones et al. 1974). It was claimed in that study that, based upon measured rates of oxygen uptake, photodegraded Ecolyte polypropylene was a nutrient source for various soil bacteria. Since polypropylene is a branched polymer with every other carbon atom in its chain bearing a methyl group, this contrasts with the results of Potts et al. who found such materials not to be biodegradable. This apparent contradiction was noted by Jones et al. who suggested that the differences might be attributable to the fact that Potts et al. "... used only a small selection of fungi (not bacteria) in their tests, and furthermore most of their polymers were not oxidized to introduce carbonyl groups."

This was also recognized by Colin et al. who wrote "Therefore a study of microbial attack on ketones rather than hydrocarbons might be most relevant to microbial attack on photodegraded polymers." (Colin et al. 1976). These authors, using a variety of middle ketones (carbonyl group in the centre of the alkane chain), were able to demonstrate microbial growth for chain lengths of up to 35 carbon atoms and molecular weights up to 507. However, their reported growth ratings, using the same scale as that employed by Potts et al., indicated significantly reduced biological activity for middle ketones of molecular weights 479 and 507 as compared to lower molecular weight materials.

In addition, similar tests were carried out on highly photodegraded polyethylene samples, including the photodegradable Ecolyte PE. In all cases it was found that "... highly irradiated LDPE samples (as well as the unirradiated controls) supported negligible growth.". These authors go on to conclude that "A complete recycling of synthetic macromolecules would require a high distribution of the UV sensitive carbonyl group along all polymer chains, followed by intensive irradiation.". These conditions are, of course, precluded by the commercial necessity of not significantly affecting either the processability or the resultant physical properties of the virgin plastics to which the photosensitizing components are added. The masterbatch approach taken by many of the carbonyl comonomer technologies requires the use of minimum needed levels of these comonomers to enhance photodegradability so that the masterbatch remains compatible with and does not affect the processability of the virgin resin. In addition, no carbonyl groups are, of course, introduced to the virgin polymer chains by addition of the masterbatch. Thus, the requirement of a high distribution of carbonyl groups along all polymer chains for complete recycling of the synthetic macromolecules, as noted by Colin et al. above, is not met with these systems.

A further examination of the seemingly contradictory claims with respect to the ultimate biodegradability of the microfragments formed by photodegradation of sensitized plastics was carried out by Cornell et al. (Cornell 1984). Polyethylene (PE), polypropylene (PP) and sensitized (for enhanced photodegradation) polyethylene (SPE) were photodegraded under a wide variety of illumination sources including sunlight. Solvent extraction of the photodegraded materials to separate out the lower molecular weight components (oligomers) was carried out. Subsequent microbial challenging of these fractions gave clear evidence for the oligomers being able to sustain microbial growth but not so the residual high polymer fractions. Further, it was necessary to remove the oligomer fractions from the polymers for them to sustain microbial growth. The polyolefin fragments, as formed by the photodegradation process showed minimal or no activity.

Cornell et al. found that photodegradation produced significant volatile fractions (up to 90% of the initial sample weight for polypropylene exposed to the output of a 550 watt high pressure mercury lamp) which are lost as possible microorganism nutrient sources. Furthermore, photodegradation led to generation of oligomer fractions which, in addition to those already present prior to irradiation, could sustain microbial growth when separated from the residual high polymer. However, irradiation of the SPE polymer did not produce oligomer levels beyond a limiting value of about 10% (w/w), based on initial sample weight, while a significant cross-linked component of up to 27.8% (w/w) was also formed. The latter was not susceptible to microbial attack and developed as a result of the continued photoirradiation of the oligomers.

The net result of the foregoing is that only a limited amount of photodegraded polymer would be suitable as a nutrient source for microorganisms. Further, only that portion of the oligomers on, or diffusing to, the surfaces of the "plastic dust" is available. The remaining oligomer is converted as it is being formed to volatiles which are lost to the atmosphere or to cross-linked material. The latter, in turn, is degraded to volatiles over time with continued irradiation. The primary degradation products, therefore, are hydrocarbon based residues which are lost to the atmosphere and not carbon dioxide and water as widely propounded in the trade literature debate.

It is noted that such contradictory studies as to the ultimate biodegradability of the photodegraded plastics have apparently not yet been encountered by all researchers in this field. As recently as 1989 the claim has been made for polyethylene grafted with vinyl acetate and acrylic monomers that the treatment "... provides a method for rendering LDPE articles photo-degradable in the short term and biodegradable in the long term." (Giesse et al. 1989). It is to be hoped that in the absence of definitive studies supporting the latter part of this statement, the frequency of its appearance in the literature decreases quickly in the near future.

11.3 Environmental Factors

Rates of degradation of the various photodegradable plastics currently commercially available are dependent upon both the amounts of sensitizing agents incorporated as well as exposure levels to ultraviolet light generally of 330 nm wavelength or less. Under controlled conditions of exposure, for example, in a laboratory experiment using a mercury lamp and appropriate light filters, the time required to achieve a given degree of polymer degradation can be closely predicted.

However, outdoors there are a large number of factors which can affect the amount of light absorbed per unit time and hence, the lifetimes of the plastics. Examples of these factors include average temperatures, rainfall and humidity leading to both amount and duration of surface and groundwater, and the wavelength distribution of the solar radiation at the particular geographic location as well as its angle of incidence. Others are the build-up of dirt on the surfaces of the plastic article and the effects of colouring pigments. For litter, the specific end location of the discarded article, for example, whether trapped in the shade of a leafy bush or hedge or relatively exposed on a rocky beach could strongly affect the "controlled" lifetime of the plastic object.

The issue of photodegradable plastics as a potential solution for pollution in the marine environment is particularly topical. The unquestionably widespread destruction of wildlife by plastics wastes has provided a powerful impulse for the mandating by various jurisdictional bodies of the use of photodegradable plastics in certain applications. However, while hard data on the environmental effects of photodegradable plastics on dry land has been difficult to locate here, no such data whatever from independent sources on degradation in marine environments was found. Claims such as "... the material degrades in salt water, but at a slower rate than in direct sunlight." (Wilder 1989) are typical.

It has already been noted above that while estimates of the extent of damage to wildlife have been made, no corresponding estimates of the reduction to be expected by the widespread use of photodegradables have been found. Indeed, the question itself has not been posed in any of the sources reviewed here.

A plastic article "programmed" to degrade within 60 days on land, for example, but degrading "at a slower rate" in seawater (100 days or longer?) would still be a hazard for at least three months. A plastic bag ingested by a sea turtle during this time would likely cause equivalent harm whether photo or non-photdegradable. While it cannot be argued that some reduction in the rates of destruction of wildlife would not occur from the use of photodegradable technologies, much more information than is currently available on the extent of this benefit is required to balance it against the possible negative effects upon alternative strategies such as education and recycling. The effects of environmental factors such as those listed at the start of this section have generally received little study in the published literature. It is interesting to note that several inventors making patent claims to an environmentally degradable material (Guiffre et al. 1976, Taylor 1977, Plank 1977, Floyd et al. 1977, Guillet 1979, Scott et al. 1986, and Rolland 1986) have reported no outdoors experiments at all in their patents. All degradation studies were carried out indoors using artificial light sources of high intensities. Where environmental studies have been carried out, the reporting of data such as hours of sunshine and its spectral distribution, average temperatures, and levels of precipitation has been done to various levels of detail. These range from simple windowsill testing (Henry 1972) for periods as short as 2 to 4 days with no information whatsoever on light intensities or total hours of exposure, to highly detailed studies (Cornell et al. 1984) wherein even changes in the intensities of the various components of the solar spectrum over a six month test period were reported.

Outdoors exposures have generally entailed loosely mounting test strips of plastics films, using either staples or nails, onto wooden frames and then placing them facing southwards at an angle of 45 degrees from the horizontal (Bremer 1982, Cornell et al. 1984, and Severini et al. 1988). The latter is considered to represent optimum exposure conditions. Others have studied the degradation of films placed horizontally, as would be the case in mulching applications (AB Akerlund & Rausing 1972, Gilead et al. 1985, and Omichi et al. 1981). No studies of angle of exposure between these two extremes and resultant degradation rates have been found here. Since one must assume that litter in the environment would be trapped in random orientations with respect to the direction of solar radiation, such studies would have importance in defining the term "controlled degradation".

The effects of reduced total light absorbance due to such factors as dirt accumulation upon the surfaces of the plastic films or articles, or location in highly shadowed areas, have also received little attention in the published literature. No controlled study of the effects of dirt accumulation was found here nor was there even any obvious reference made to the issue. A similar situation pertained to the effects of shade although this was in some cases directly recognized as a factor in delaying photodegradation. For example, Gilead et al. write, with respect to their test methodology, that "The films were unshaded throughout: obviously if they had been shaded by existing vegetation or by growing crops, they would have required a longer time to receive the same amount of radiation." (Gilead et al. 1985). No indication is given of how much longer this would be nor were such experiments carried out.

Similarly, Omichi et al. studied the photodegradation of modified polyethylene films as mulches over seedbeds of strawberry plants in both indoor (greenhouse) and outdoor locations (Omichi et al. 1981). Only samples of films taken from locations not shadowed by strawberry leaves were chosen for the testing of the extent of degradation. The simultaneous testing of film specimens located in highly shaded areas, which would have been quite simple to do and would have provided highly useful additional comparative data was not done. This is considered here to be most unfortunate.

Finally, many commercial plastic articles which become litter are coloured with various pigments. In addition, some items such as chocolate bar wrappers may have a foil layer to increase the lifetime of the contents. Indeed, the issue of the possible effects of such newer, low gas permeability laminates used in a growing number of packaging applications has not been found to be addressed in the literature. With respect to pigmentation itself, again very little appears in the reviewed literature. The interesting situation of possibly being able to make valid claims, under current definitions, of photodegradability for a simple mix of low density polyethylene with brown iron oxide pigments has already been commented upon. Scott et al. note that the incorporation of carbon black, which acts as an ultraviolet light stabilizer, would extend the time required to reach embrittlement (Scott et al. 1986). This should not be a significant factor as carbon black is not widely used in packaging applications. However, no studies on the comparative effects of titanium dioxide, a very common white pigment which is widely used in packaging materials have also been found. While the anatase form of this pigment is known to be catalytic in the photodegradation of plastics materials containing it, the far more widely used rutile form is not. Indeed, due to its very high light reflectivity, the latter may promote photostability of the plastic matrix by reducing the total amount and depth of light absorption.

11.4 Exposure Test Methodology

This section of the current report will deal with test methods used to study photodegradation of plastics in non-outdoors environments. Typical procedures used to assess breakdown under outdoors conditions have already been discussed in the preceding section. Test methodologies may be broadly broken down into two general categories as in those for studies intended to be published in the anonymously peer reviewed scientific literature and in those for purposes of patent claims.

The first case, studies for the scientific literature, tends to be characterized by the availability of much more detailed information on both materials used and experimental protocols followed. For example, the polymers of interest would have more complete data reported for such things as overall composition, concentrations of photosensitive species or functionalities, average molecular weights and molecular weight distributions and light absorbance characteristics in the wavelength region of interest. Changes in these properties as a function of total absorbed irradiation would be reported in more detail and would generally be fit to some proposed chemical mechanistic pathway.

A typical experiment would see photosensitive plastic films exposed to a narrow wavelength band of light isolated by the use of appropriate glass or chemical filters from the total output of, for example, a high pressure mercury lamp. The angle of light incidence would nearly always be perpendicular to the films in order to minimize corrections for such phenomena as increased path lengths in the films due to internal reflectance or to loss of incident radiation due to front face reflection. In addition, the films would be contained in sealed chambers which would permit the use of various inert gas atmospheres as well as oxygen, in conjunction with maintaining tight temperature control of the samples.

Periodically, the exposed films would be monitored for properties of interest such as carbonyl growth using infrared or ultraviolet

spectroscopy or for the number of chain breakages incurred using either viscosity measurements or determination of molecular weights using size exclusion (gel permeation) chromatography. Volatiles could be swept out of the sealed chamber, trapped and subsequently analysed by gas chromatography/mass spectrometry. Quantification of these events or byproducts formed, in conjunction with a knowledge of the irradiation intensity incident upon the samples as well as the absorbance characteristics of the films at the wavelengths being used, allows the calculation of quantum yields. The latter is defined in many ways but most generally as the probability of occurrence of an event of interest per photon of light absorbed. Changes in quantum yields as a function of temperature allows the calculation of activation energies for chemical processes of interest, such as chain scission. The use of small molecules capable of quenching (deactivating) the excited state chromophores enables one to determine the lifetimes of the latter, assuming a reliable diffusion rate constant for the quencher molecule in the bulk polymer matrix is known. Alternatively, excited state lifetimes may be measured directly using techniques such as single photon counting or laser flash spectroscopy. Such studies allow a high degree of knowledge to be generated for the photodegradative pathways of the irradiated films. However, it must be kept in mind that this information pertains to the processes as observed under highly "artificial" conditions. The use of constant light intensities of narrow wavelength distributions does not mimic an outdoors environment. The same would apply to the angle of incidence of the light onto the films and the constant temperatures. Wind, rain, and soil effects are obviously absent. The correction of the results of such highly controlled experiments for the environmental factors discussed in the immediately preceding section of this review in order to achieve a high degree of predictability under open air conditions has not been accomplished to date.

In terms of byproduct analysis, such laboratory experiments have an additional drawback. In order to complete experiments in a reasonably short time, relatively high intensities of incident light are used. For example, the intensity of the 254 nm light from a high pressure mercury lamp is several orders of magnitude higher than the intensity of this same wavelength of light reaching the earth's surface from the sun. Small molecule byproducts could, therefore, easily be subjected to additional, photochemically induced reactions before they have the chance to diffuse to the surface of the film and escape. Comparison of the results from these short term, high light intensity experiments to those from long term studies wherein films were irradiated with narrow band light but of an intensity more closely approximating those reaching the earth's surface at any given geographical location would be most interesting. Unfortunately, such studies do not appear to have been carried out.

Experimental protocols for the purposes of patent claims do not appear, in general, to approach the levels of sophistication seen in the scientific literature. For accelerated aging studies, the most commonly used test methodology entails exposure in a weather-ometer. The latter is a unit consisting of a high intensity light source centrally located in an enclosed chamber. Samples to be exposed are mounted upon a merry-go-round which circles the light source and ensures that all test specimens receive identical exposures. Both carbon arc and xenon arc light source weather-ometers have been used. The former has generally been replaced by the latter in terms of modern usage as the xenon arc is simpler to maintain and its spectral output more closely matches that of the solar radiation reaching the earth's surface. Black panel temperatures are rarely specified in the patent literature even though test specimens may reach temperatures as high as 50 C in such units. In addition, the use of a water cycle (which these instruments are capable of providing) is not mentioned in any of the patents reviewed here.

Following exposure in the weather-ometer, degradation of the plastic films has been most often monitored by infrared spectroscopy (determination of the carbonyl index) or by changes in physical properties such as tensile strength and percent elongation at break using an Instron apparatus or equivalent. Such physical measurements are at best, as is well known to those experienced in the field, relatively blunt instruments for determining the extent of change in a material in thin film form. This is reflected in the decay curves of the physical properties as seen in the patent literature wherein actual data points are omitted in favour of smooth lines (Gilead et al. 1985) or even when such decay curves are not given at all as is the case in general.

In summary, although some commonality of test procedures exists, there are sufficient variations from protocol to protocol to make correlation difficult if not impossible. Neither tightly controlled laboratory experiments nor more loosely structured testing in such accelerated aging units as weather-ometers provides adequate data to enable prediction of in-field performance to be made with any degree of confidence. The knowledge base enabling such claims as "controlled" or "programmed" or "timed" to be made relative to photodegradable plastics deterioration rates in outdoors environments does not appear to have been developed by independent research and reported in the literature.

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APPENDIX A

AGRIBUSINESS U.S.A.SM

Coverage: 1985 to the present

It provides current access to agricultural business information, which is utilized for strategic planning in many industries. The AGRIBUSINESS U.S.A. database covers all facets of agribusiness such as the crop and livestock industries, agricultural chemicals biotechnology, agricultural finance, farm equipment manufacturing, and agricultural marketing. The database is designed to track U.S. and regional agribusiness information, including company names, trade names, new product development, and government policies.

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Coverage: 1970 to the present

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ANALYTICAL ABSTRACTS is devoted to all aspects of analytical chemistry: any general applications, inorganic chemistry, organic chemistry, pharmaceutical chemistry, environmental agriculture, and more. The database contains references from approximately 1,300 journals, 300 of which are core journals, as well as information gathered from conference papers, books, standards, and technical reports. Information found in a record from ANALYTICAL ABSTRACTS includes chemical names, including synonyms and/or trade names, CAS Registry Numbers, analyte and matrices information, and more.

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Biotechnology Abstracts file provides detailed coverage of all aspects of biotechnology from agricultural use to pharmaceuticals, including genetics, downstream processing, and more.

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The CA SEARCH database includes citations to the literature of chemistry and its applications. CA SEARCH is an expanded database which contains the basic bibliographic information appearing in the print *Chemical Abstracts*. Complete index entries contain CA General Subject headings from a controlled vocabulary, and CAS Registry Numbers, that are unique numbers assigned to each specific chemical compound.

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CHEMICAL ENGINEERING ABSTRACTS (CEA) provides information on industrial practice and theoretical chemical engineering. The abstracts contained in the database cover the processing of chemicals, including chemical reactions, mixing or separation, heating or cooling, or transport. The effects of the size of the operation, the physical and other properties of the substances involved, the nature of the equipment used, and safety factors, are all subjects likely to be covered in CEA abstracts.

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The FEDERAL RESEARCH IN PROGRESS (FEDRIP) database provides access to information about ongoing federally funded research projects in the fields of physical sciences, engineering, and life sciences; research information is provided to NTIS by the sponsoring U.S. government agencies. Most records also include a description of the research, although the exact record content varies according to the sponsoring agency.

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Coverage: 1969 to the present

FOOD SCIENCE AND TECHNOLOGY ABSTRACTS (ESTA) provides access to research and new development literature in the areas related to food science and technology. Allied disciplines, such as agriculture, chemistry, biochemistry, and physics are also covered. Related disciplines such as engineering and home economics are included when relevant to food science. Information in this database supports research by scientists, technologists, marketing personnel, teachers, and scholars working in areas related to food science and technology.

FOODS ADLIBRA™

Coverage: 1974 to the present

FOODS ADLIBRA™ contains up-to-date information on the latest developments in food technology and packaging. FOODS ADLIBRA provides information on every sector of the food industry including retailers, processors, brokers, equipment suppliers, gourmet food importers, as well as general company and food association news.

INSPEC

Coverage: 1969 to the present

The *Science Abstracts* family of abstract journals, indexes, and title bulletins commenced publication in 1898. Today it forms the largest English-language database in the fields of physics, electrotechnology, computers and control, and information technology. The online INSPEC file corresponds to the printed *Physics Abstracts, Electrical and Electronics Abstracts, Computer and Control Abstracts*, and *IT Focus*. Non-English-language source material is also included, but abstracted and indexed in English.

The principal subject areas are indicated by the major headings of the classification approach used for the INSPEC databases (e.g. Atomic and Molecular Physics; Computer Programming and Applications; Computer Systems and Equipment; and Elementary Particle Physics).

LIFE SCIENCES COLLECTION

Coverage: 1978 to the present

LIFE SCIENCES COLLECTION contains abstracts of information in the fields of animal behavior, biochemistry, ecology, endocrinology, entomology, genetics, immunology, microbiology, oncology, neuroscience, toxicology, and virology among others, and corresponds to the series of 17 abstracting journals.

MATERIALS BUSINESS FILE

Coverage: 1985 to the present

MATERIALS BUSINESS FILE covers technical and commercial developments in iron and steel, nonferrous metals, composites, plastics, etc. Subjects covered are grouped into 9 categories: 1) Fuel, Energy Usage, Raw Materials, Recycling; 2) Plant Developments and Descriptions; 3) Engineering, Control and Testing, Machinery; 4) Environmental Issues, Waste Treatment, Health and Safety; 5) Product and Process Development; 6) Applications, Competitive Materials, Substitution; 7) Management, Training, Regulations, Marketing; 8) Economics, Statistics, Resources, and Reserves; and 9) World Industry News, Company Information, and General Issues.

NTIS

Coverage: 1964 to the present

The NTIS database consists of government-sponsored research, development, and engineering plus analyses prepared by federal agencies, their contractors, or grantees.

This database covers a wide spectrum of subjects including: administration and management, agriculture and food, behavior and society, building, business and economics, chemistry, civil engineering, energy, health planning, library and information science, materials science, medicine and biology, military science, transportation, and much more.

PACKAGING SCIENCE AND TECHNOLOGY ABSTRACTS

Coverage: 1982 to the present

PACKAGING SCIENCE AND TECHNOLOGY ABSTRACTS provides access to research and development literature in all aspects of packaging science, including materials, equipment, packs, transport, storage, and testing.

PASCAL

Coverage: 1986 to the present

PASCAL represents the merger of two different databases, PASCAL M and PASCAL S, PASCAL M is multidisciplinary, covering the core of world scientific and technical literature. PASCAL S consists of ten subject specialty files which provide exhaustive coverage; these files are produced in cooperation with specialist organizations in each of the disciplines covered.

PIRA ABSTRACTS

Coverage: 1975 to date

PIRA provides abstracts of the scientific and technical literature in paper, board, printing and packaging industries. A constant and thorough surveillance of the world's specialist literature is derived from PIRA's extensive bibliographic and database resources.

POLLUTION ABSTRACTS

Coverage: 1970 to the present

POLLUTION ABSTRACTS is a leading resource for references to environmentally related literature on pollution, its sources, and its control. The following subjects are covered by the POLLUTION ABSTRACTS database; air pollution, environmental quality, noise pollution, pesticides, radiation, solid wastes, and water pollution.

PTS PROMT

Coverage: 1972 to the present

PTS PROMT (*Predicasts Overview of Markets and Technology*) abstracts all significant information appearing in thousands of newspapers, business magazines, government reports, trade journals, bank letters, and special reports throughout the world.

The PROMT database provides the following kinds of information: acquisitions, capacities, end uses, environment, international trade, market data, new products, production, regulations, and technology. The information covers products and services of the following industries: chemical, communications, computers, electronics, energy, fibers, food, instruments and equipment, metals, paper, plastics, and rubber.

RUBBER & PLASTICS ABSTRACTS (RAPRA)

Coverage: 1972 to date

The RAPRA abstracts database covers all commercial and technical information on polymer materials, processing and products. The database corresponds to the hard copy publication RAPRA Abstracts. The database covers the world's polymer literature including journals, conference proceedings, books, specifications, reports and trade literature. Patents were included from 1978-80.

SCISEARCH®

Coverage: 1974 to the present

SCISEARCH® is a multidisciplinary index to the literature of science and technology prepared by the Institute for Scientific Information (ISI). SCISEARCH covers every area of the pure and applied sciences.

SUPERTECH (formerly TELEGEN™)

Coverage: 1973 to the present

SUPERTECH consists of five subfiles with information related to fields of biotechnology, artificial intelligence, computer-aided design/computer-aided manufacturing (CAD/CAM), robotics, and telecommunications.

WATER RESOURCES ABSTRACTS

Coverage: 1968 to the present

WATER RESOURCES ABSTRACTS (WRA) is prepared from materials collected by over 50 water research centers and institutes in the United States. The file covers a wide range of water resource topics including water resource economics, ground and surface water hydrology, metropolitan water resources planning and management, and water-related aspects of nuclear radiation and safety. The collection is particularly strong in the literature on water planning (demand, economics, cost allocations), water cycle *(precipitation, snow, groundwater, lakes, erosion, etc.), and water quality (pollution, waste treatment).

PLASTICS DEGRADABILITY

WHY DEGRADABILITY

The growing world wide concern over solid waste has caused a great deal of attention to be focussed on plastics, which are perceived to be non "degradable". Products are now being marketed which claim to address this perceived deficiency in plastics, and while these products will find some applications, they are by no means a universal solution to the plastics waste problem. A lack of understanding of the waste and litter problem has created a great deal of confusion in the minds of the general public. The roles that "degradable plastics" can and cannot play are discussed below.

WHAT IS DEGRADABILITY

All plastics deteriorate and break down over time. Scientists have expended a great deal of effort, over the years, to improve the durability of plastics and extend the useful life of plastic products. Much of the durability improvement is achieved with the use of additives.

The new products offered as degradable are in fact designed to do the very opposite i.e. speed up the degradation or breakdown of the product.

Two general types of degradable products are being offered. Photodegradable products exhibit accelerated degradation when exposed to sunlight. Products which are commonly called biodegradable contain cornstarch which depends on the action of micro organisms, and other chemicals, which promote breakdown of the plastic. In both cases, under the correct conditions, it results in the breakdown of the plastic article into ever smaller pieces.

EFFECT ON LITTER

Litter is the result of irresponsible or accidental disposal of products. The ideal way to eliminate litter is to eliminate the littering behaviour through education and deterents such as fines, and to identify and correct the causes of accidental littering.

Given that litter does occur, it contributes to visual pollution and poses a potential threat to wildlife. In addition to education to change behaviour, there is a need to either collect the litter or to reduce the longevity of littered items.

While there is currently no legislation in Canada, in many foreign jurisdictions (i.e. Italy, Florida), certain plastic packaging materials are being mandated to lose properties (degrade) within specified time frames (within120 days for polyethylene, within one year for polystyrene, etc.)

Photodegradable products can have a positive impact on plastics litter in both land and marine situations. The breakdown of plastics is triggered by ultra violet radiation from the sun. The effectiveness is dependent on exposure intensity and will vary with factors such as the season, geography, dirt or water cover, shading, etc. The question of whether making plastics degradable will encourage littering has frequently been asked but remains unanswered.

Available commercial biodegradable products are not being promoted for litter management due to the significant difficulties in consistently achieving the needed conditions for biological activity.

EFFECT ON LANDFILL

Degradation is generally a complex and slow process. For a material to biodegrade, it must be exposed to the correct combination of acidity, temperature, nutrients, particle size, moisture, air and bacteria. Under modern landfill conditions, many materials generally regarded as degradable (i.e. food, yard waste, paper, etc.) deteriorate either slowly or not at all. Coatings or heavy printing further slow down the degradation rate.

Photodegradable plastic systems are not being promoted as a means to reduce landfill because the ultra violet light needed to cause degradation is not present.

Under the correct conditions, the physical properties of plastics containing biodegradable additives can be reduced. However, sanitary landfills are typically run in a "dry" mode (i.e. clay cap, removal of leachate). This results in insufficient moisture for large scale degradation to occur.

In view of these conditions, the addition of biodegradable materials of any type will not extend the useful life of landfill sites.

PRODUCTS OF DEGRADATION

There have been questions raised about the environmental impact of the products of degradation and the increased rate at which additives such as pigments are released. These issues are being addressed through both supplier and industry-backed studies.

COMPATABILITY WITH RECYCLING

Questions have been raised about the compatability of degradable systems with recycling. The questions relate to the processability of the recycled plastics as well as possible reduced life of products made from recycled plastics. The effects depend on which degradable system is used, the type of recycling process, as well as the end product. These concerns are being addressed through further research.

ECONOMIC IMPACT

The use of degradable systems adds cost. The actual cost increase depends on the application and system chosen. The major cost increase components are in the cost of the additive system and, in the case of the biodegradable product, there may be additional plastic resin required.

QUALITY

The industry is concerned about the lack of recognized performance standards governing the use of degradable plastics. The Society of the Plastics Industry is working with organizations such as the Canadian Standards Association to address this need.

SUMMARY

Degradable plastics offer benefits in selected applications. Photodegradability may be useful in products with high litter potential. Biodegradable products may be beneficial in products which are not going to be recycled and which will be disposed of under conditions conducive to biodegradation. Research is continuing to determine the environmental acceptability of the products of degradation, and the impact on recycling and people's tendency to litter. It is important to recognize that degradability is only one component of responsible solid waste and litter management.

EPIC

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